

NASA  
Upper  
Atmosphere  
Research  
Program

**RESEARCH  
SUMMARIES**

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**NASA**

National Aeronautics and  
Space Administration  
Washington, D.C. 20546

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NASA Upper Atmosphere  
Research Program

# RESEARCH SUMMARIES

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Report to the Congress and the  
Environmental Protection Agency on the  
National Aeronautics and Space Administration  
Upper Atmosphere Research Program

JANUARY 1992





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## INTRODUCTION



## INTRODUCTION

In compliance with the Clean Air Act Amendments of 1977, P. L. 95-95, the National Aeronautics and Space Administration (NASA) has prepared a report on the state of our knowledge of the Earth's upper atmosphere, particularly the stratosphere, and on the progress of the NASA Upper Atmosphere Research Program (UARP). The report is composed of two parts. Part I is the present document, which summarizes the objectives, status, and accomplishments of the research tasks supported under the NASA UARP. Part II is an assessment entitled "Present State of Knowledge of the Upper Atmosphere: An Assessment Report" which will be issued in May, 1992. It consists primarily of the Executive Summary and Chapter Summaries of the World Meteorological Organization Global Ozone Research and Monitoring Project Report No. 25 "Scientific Assessment of Stratospheric Ozone: 1991" sponsored by NASA, the National Oceanic and Atmospheric Administration (NOAA), the UK Department of the Environment, the United Nations Environment Program, and the World Meteorological Organization. Other sections of part II include: the end of mission statement for the NASA/NOAA Second Airborne Arctic Stratospheric Expedition (AASE II) and the most recent evaluation of photochemical and chemical kinetics data (Evaluation No. 10 of the NASA Panel for Data Evaluation) used as input parameters for atmospheric models.

Under the mandate contained in the FY 1976 NASA Authorization Act, NASA has developed and is implementing a comprehensive program of research, technology, and monitoring of the Earth's upper atmosphere, with emphasis on the stratosphere. This program focuses on expanding our understanding of this important region of our atmospheric environment and on developing an ability to assess potential perturbations, particularly to the ozone layer. The NASA UARP is managed within the Earth Science and Applications Division in the Office of Space Science and Applications. The long-term objectives of the present program are to perform research to:

- a. understand the physics, chemistry and transport processes of the upper atmosphere, and
- b. accurately assess possible perturbations of the upper atmosphere caused by human activities as well as by natural phenomena.

The NASA program supports a variety of research tasks proposed by scientists from the university, government, and industrial research communities. The UARP also sponsors periodic assessments of the state of our knowledge of the stratosphere and its response to specific perturbations such as chlorofluoromethane (CFM) releases, aircraft effluents, and other potential pollutants. Of greatest urgency at present is an assessment of the combined effects of continued increases in the atmospheric concentrations of  $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CF}_3\text{Br}$ ,  $\text{CF}_2\text{ClBr}$  and other halocarbons,  $\text{CO}_2$ ,  $\text{NO}_x$ , and other gases such as  $\text{N}_2\text{O}$  and  $\text{CH}_4$ . Another goal is to understand the role of stratospheric ozone in the radiative heating and dynamics of the atmosphere and, thereby, to assess the importance of chemical-radiative-dynamical feedbacks on the meteorology and climatology of the stratosphere and troposphere. Other tasks involve the analysis of data obtained by large satellite missions such as SAGE I and II and Nimbus-7, and by aircraft campaigns such as the Stratosphere Troposphere Exchange Project (STEP), the Airborne Antarctic Ozone Experiment (AAOE), and the first and second Airborne Arctic Stratospheric Expeditions

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(AASE I & II). In addition, it supports laboratory and field measurement activities for the analysis and interpretation of data from the Upper Atmosphere Research Satellite (UARS) launched September 12, 1991. In the portion of the program other than direct satellite missions, activities fall into four broad categories: (1) field measurements (employing in-situ and remote sensing techniques from ground-based, aircraft, balloon, and rocket platforms); (2) laboratory studies (gas phase and heterogeneous kinetics, photochemistry, spectroscopy, and calibration standards development); (3) theoretical studies (1-D, 2-D, and 3-D models of photochemistry and dynamics); and (4) data analysis (especially analyses of large satellite data sets). Funding of the research program was approximately \$28M in FY 91. Since the 1990 report, substantial advances in our knowledge of the upper atmosphere have been made in each of the four major research categories. Laboratory studies (particularly in the area of heterogeneous reactions) have strengthened our knowledge of the chemical kinetics of stratospheric components, and have provided improved data on the spectroscopy of atmospheric gases for applications to atmospheric measurements of trace species. Many of the trace gases in the hydrogen, nitrogen, and chlorine chemical families which participate in the chemistry of ozone have been detected in the stratosphere and detailed information on their spatial and temporal variations is becoming more available. Current research funding supports specific investigations dealing with the following topics:

- a. Determination of the distribution of trace gases in the stratosphere, with emphasis on those species which influence the ozone balance.
- b. Observations of the global distribution of ozone, its vertical profile, and temporal variations. A key initiative in this area is the implementation of a ground-based remote-sensing measurement Network for the Detection of Stratospheric Change (NDSC).
- c. Determination of the geographic distribution and strengths of the sources and sinks for stratospheric compounds. A strong focus in this area is associated with chlorofluorocarbon alternatives, namely the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs).
- d. Development of more realistic multi-dimensional models of the stratosphere and troposphere.
- e. Application of 2-D and 3-D stratospheric models to assess the impacts of changing atmospheric composition. Specific emphasis is being placed on assessing the impact of high speed aircraft on stratospheric ozone and chemistry.
- f. Utilization of theoretical models to develop a strategy for detecting change in atmospheric ozone.
- g. Improvements in the understanding of atmospheric dynamics and transport processes by both theory and measurement.
- h. Validation of theoretical models by comparison with atmospheric measurements.



- i. Measurements of the ultraviolet solar irradiance and its temporal variations.
- j. Determination of the mechanisms responsible for exchange of air between the troposphere and stratosphere.
- k. Laboratory studies in spectroscopy and chemical kinetics relevant to the interpretation of atmospheric measurements and to theoretical simulation of the atmosphere.
- l. Development of new technological ideas, techniques, and instruments for use in upper atmospheric research.

There are several activities during 1990 and 1991 that should be highlighted. In general they each involved an integration of several facets of the research supported by the UARP. These include:

1. **An extended analysis of the data from the Airborne Arctic Stratospheric Expedition conducted in late 1989.** This analysis has better quantified the extent of ozone loss associated with the high concentrations of reactive chlorine and bromine measured during this mission. It also has served as a basis for formulating the measurement strategy for a more extended investigation of the northern hemisphere mid and high latitude stratosphere as discussed below.
2. **The Second Airborne Arctic Stratospheric Expedition (AASE-II).** This measurement campaign, formulated on the basis of results of the 1989 Airborne Arctic Stratospheric Expedition (AASE) and conducted from October, 1991 to March, 1992, was designed to address the specific issues: 1) Will significant erosion of the Earth's stratospheric ozone shield occur over the Arctic region as stratospheric chlorine concentrations increase during the next decade? 2) What are the causes of widespread stratospheric ozone decreases over mid-latitudes in winter through early summer revealed over the past decade by satellite and ground-based observations? and 3) What effect does volcanic debris have on chemical processes that govern stratospheric ozone concentrations? In particular, could volcanic aerosols amplify depletion of stratospheric ozone associated with anthropogenic emissions?
3. **A reanalysis of total column ozone and vertical distribution of ozone data.** Since the 1990 report the observational record includes an additional 2.5 years of SAGE and TOMS data. This is complemented by a major new advance of an internally calibrated TOMS data set (version 6) that is independent of ground-based observations. Trend analyses of SAGE data have now been extended to the lower stratosphere. Ground-based and satellite (TOMS) observations of total column ozone through March, 1991 have been analyzed, allowing for the influence of solar cycle and quasi-biennial oscillation to be removed from any other trend.

4. **Completion of the latest international assessment of stratospheric ozone.**  
NASA and the National Oceanic and Atmospheric Administration (NOAA) coordinated the "Scientific Assessment of Stratospheric Ozone: 1991" co-sponsored by the United Nations Environment Program, the World Meteorological Organization, and the United Kingdom Department of Environment. This assessment was one of three conducted under the provisions of the Montreal Protocol on Substances that Deplete the Ozone Layer. It serves as the scientific basis for assessing and modifying the control measures of the Protocol.
5. **Implementation of the Network for the Detection of Stratospheric Change (NDSC).** An international meeting formally establishing the organizational structure of the NDSC was held in Geneva, Switzerland in November of 1989. The Network is a set of high quality research stations for observing and understanding changes in the physical and chemical state of the stratosphere that are complemented by secondary stations and satellite measurements and are coordinated with other networks. The NASA UARP (together with NOAA and the Chemical Manufacturers Association) have been supporting the development of the state-of-the-art instrumentation with which such stations will be equipped. The NDSC Steering Committee met in Cambridge, UK in June, 1991 to decide on issues such as site selection, instrument evaluation and calibration, data analysis and archiving, etc. A fully implemented NDSC will serve as a focal point for future ozone trends determinations.

## I. FIELD MEASUREMENTS

- A. BALLOON-BORNE IN-SITU MEASUREMENTS
- B. BALLOON-BORNE REMOTE MEASUREMENTS
- C. GROUND-BASED MEASUREMENTS
- D. AIRCRAFT-BORNE MEASUREMENTS
- E. ROCKET-BORNE MEASUREMENTS
- F. INSTRUMENT DEVELOPMENT



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A. BALLOON-BORNE IN-SITU MEASUREMENTS

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**Measurement of Trace Stratospheric Constituents with a  
Balloon Borne Laser Radar**

Principal Investigator: William S. Heaps  
NASA/Goddard  
Code 915  
Greenbelt, MD 20771  
(301) 286-5106

Co-Investigator: Thomas J. McGee

The objective of this research has been to measure the altitude and diurnal variation of the hydroxyl radical and related chemical species in the stratosphere. Although hydroxyl has a very significant role in the chemistry of stratospheric ozone little is known about its behavior because its extremely low abundance has made it very difficult to observe. The approach we have used is a laser radar system operating from a balloon platform which measures hydroxyl by exciting the molecule to fluorescence and observing the intensity of this fluorescence.

The instrument was destroyed in an accident during a flight conducted in June, 1989. Efforts this past year have centered on refining the analysis of data obtained on the previous flights. This work is nearing completion.

This research will result in two additional publications:

Hydroxyl Radical Profiles in the Middle Atmosphere, by Wm. S. Heaps, T. J. McGee, and J. J. Butler has been submitted to JGR and is currently undergoing revision. (The title probably will change in its final form.)

The Diurnal Variation of Stratospheric Hydroxyl Radical, by Wm. S. Heaps, T. J. McGee, and J. J. Butler is currently in preparation.

## OZONE MEASUREMENTS

Principal Investigator: J. J. Margitan  
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### Objective:

Under this task, the stratospheric abundance of ozone is measured using an in situ UV absorption instrument flown piggyback aboard balloon flights launched from NSBF. The dual channel UV photometer obtains ozone profiles on ascent and descent with 1-10 second time resolution (5-50 meters) with an accuracy of 3%. These measurements aid in understanding the distribution of ozone in the stratosphere, particularly the upper stratosphere near 40 km, as well as providing complementary and comparative data for other instruments. The PI also participates as a co-investigator for the NOAA ER-2 ozone instrument for the Polar Ozone Campaigns.

### Results:

The fourth flight of the UV photometer was aboard the JPL gondola carrying the JPL Mark IV interferometer on October 8, 1989 from Ft. Sumner, NM. The ozone profile measured in situ on ascent is being compared to the profile retrieved by the Mark IV at sunset.

In the spring of 1990 the photometer was flown aboard the JPL "stacked" gondola housing the JPL Balloon Microwave Limb Sounder (BMLS) and the Far IR Limb Observing Spectrometer (FILOS) and the Smithsonian Astrophysical Observatory's Far IR Spectrometer (FIRS-2). For this flight, the GSFC trailer mounted ozone lidar was stationed nearby in order to compare lidar ozone profiles with the balloon instruments. On the May 12, 1990 flight, however, the 40 million cubic foot balloon failed at 70,000 ft., precluding the upper stratospheric comparison. A reflight of the balloon payload occurred on June 4, 1990, a few days after the lidar operation was discontinued. Nonetheless, structure observed by the UV photometer on the May 12 flight provided an interesting comparison to the lidar in the 15-20 km region, and the full profile obtained in the June 4 flight compares well with the lidar observations a few days earlier.

In the fall of 1990 the ozone instrument flew piggyback with the Mark IV interferometer and FILOS on a flight from Ft. Sumner, NM on September 27, 1990, augmenting the comparison from the previous fall.

In spring 1991, the ozone photometer flew with FILOS and the new Submillimeter Limb Sounder (SLS), on an April 9, 1991 flight from Daggett, CA (near Barstow), as a precursor of flight activity planned for the UARS Correlative Measurement Program. In addition to the comparison of ozone profiles between the balloon photometer and the SLS, the nearby JPL ozone lidar at Table Mountain, CA was operated on the night of launch,



affording an opportunity to compare lidar and in situ ozone near 40 km. As a result of that comparison, Table Mountain lidar profiles corresponding to the earlier balloon flights are being investigated. Despite the 1500 km separation for those comparisons, they show extremely good agreement, which is not totally unexpected given the limited variability typically seen in mid- and upper stratospheric ozone during the summer.

#### Publications:

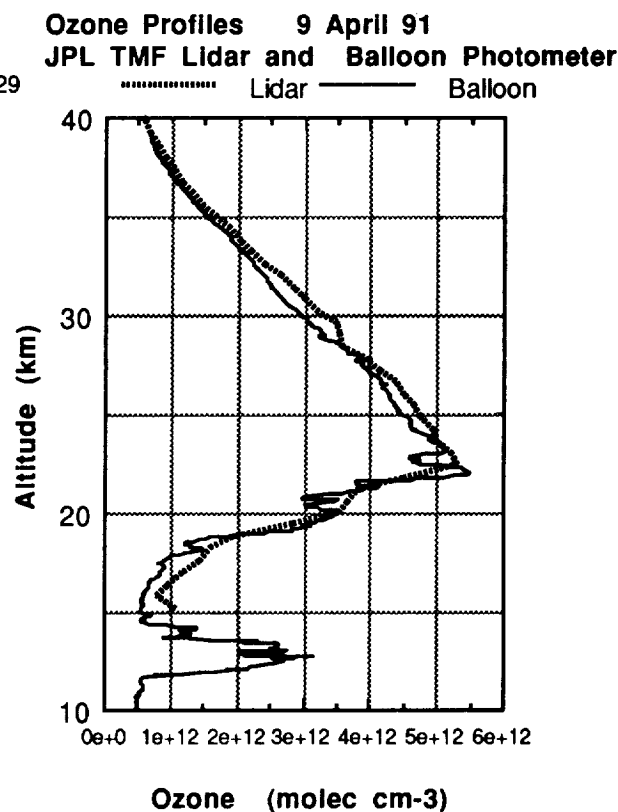
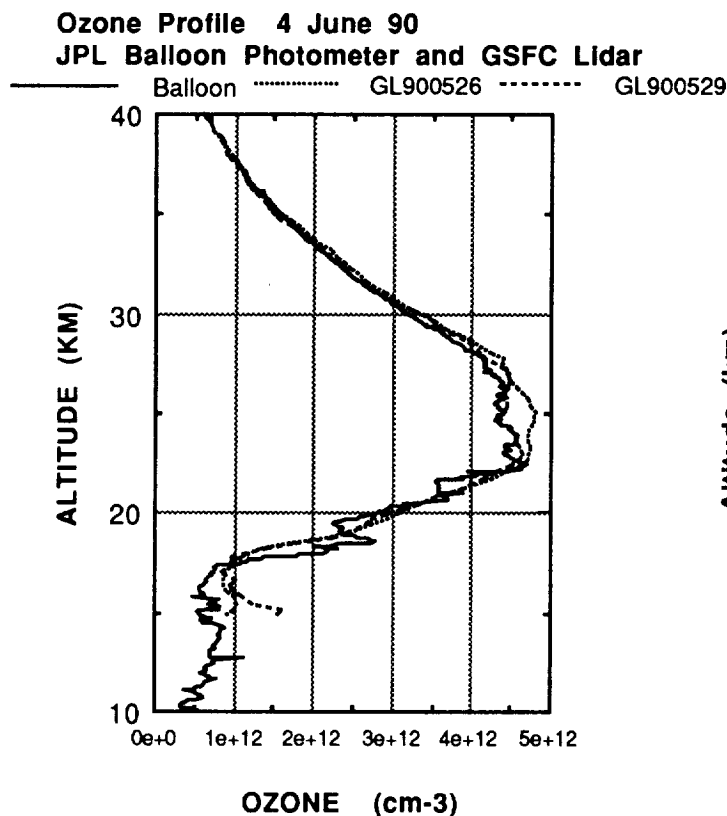
L. R. Lait, M. R. Schoeberl, P. A. Newman, M. Loewenstein, J. R. Podolske, S. E. Strahan, K. R. Chan, B. Gary, J. J. Margitan, E. V. Browell, M. P. McCormick, and A. Torres, "Reconstruction of O<sub>3</sub> and N<sub>2</sub>O Fields from ER-2, DC-8, and Balloon Observations," *Geophys. Res. Lett.* **17**, 521-524, 1990

A. R. Douglass, R. B. Rood, R. S. Stolarski, M. R. Schoeberl, M. H. Proffitt, J. J. Margitan, M. Loewenstein, J. R. Podolske, and S. E. Strahan, "Global Three-Dimensional Constituent Fields Derived from Profile Data," *Geophys. Res. Lett.* **17**, 525-528, 1990

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## A. Neutral Constituent Measurement in the Stratosphere

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C. Research objectives: Measurements of major and minor neutral constituents in the middle and upper stratosphere using a mass spectrometer or sample collection system. Laboratory studies of ozone's chemical and physical properties, the enhancements of the heavy isotopes. Laboratory studies simulating polar stratospheric cloud particles, condensation of nitric acid trihydrates (NAT), solubility of HCL in ice and NAT's.

D. Summary of Progress and Results: The studies of ozone's fundamental physical and chemical properties have continued. Substantial progress has been made in the understanding of the unusual isotope enhancement in stratospheric ozone, reported for the first time by this group in 1981.

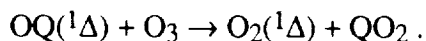
A new ozone (and CO<sub>2</sub>) collector system has been flown three times on board a balloon gondola and has provided the most accurate isotope enrichment measurements of both <sup>49</sup>O<sub>3</sub> and <sup>50</sup>O<sub>3</sub>. It appears now that there exists a 'regular' enhancement in the heavy isotopes which agrees well with results from laboratory studies. At stratospheric temperatures this enhancement is about 8-9% for both <sup>49</sup>O<sub>3</sub> and <sup>50</sup>O<sub>3</sub> above statistically predicted values. Laboratory studies have clearly established that this 'regular' enhancement is produced during the ozone formation process; its temperature and pressure dependence has been measured. In one of the collector flights, however, and in some of the mass spectrometer and infrared measurements, additional enhancements have been observed, at some altitudes exceeding 40%.

The oxygen isotopes of the separately collected CO<sub>2</sub> samples have been analyzed and compared with CO<sub>2</sub> samples collected in the troposphere. Surprisingly, a mass-independent enhancement in both <sup>17</sup>O and <sup>18</sup>O of about 11‰ was found. Yuk Yung (Caltech) and co-workers recently proposed a mechanism for transferring the heavy ozone enhancement to CO<sub>2</sub>. This pathway of oxygen transfer has been confirmed by the measurements.

Ozone research involving optical spectroscopy has focused on three principal tasks: 1) to determine adiabatic energies of ozone's lower-lying electronic states, particularly those which may affect the formation of ozone; 2) to test proposed mechanisms leading to heavy ozone anomalies; and 3) to make accurate measurements of ozone absorption cross sections in the visible region.

1) We have so far investigated the states responsible for the visible (Chappuis) and near-IR (Wulf) bands, and plan to examine even lower energy features in the near future. These energies were measured by recording absorption spectra for <sup>16</sup>O<sub>3</sub> and for <sup>18</sup>O<sub>3</sub> to determine isotope shifts for the vibronic features. Since full substitution changes all the atomic masses by the same factor, changes in the vibrational manifold are predictable. Recent results have shown that the Chappuis band arises from two states, at adiabatic energies of 2.05 and 1.95 eV, while the lowest energy features of the Wulf bands can be associated with a state of 1.24 eV. These values are in excellent agreement with the results of very recent *ab-initio* calculations from the Los Alamos group and others.

2) Yuk Yung recently proposed a new mechanism for the formation of heavy ozone. This mechanism is unique in that it does not involve production of ozone through the O + O<sub>2</sub> + M reaction, but rather the modification of the isotopic populations through isotope exchange between excited oxygen and ozone:



The proposed mechanism required the rate coefficient to be at least  $5 \times 10^{-14}$  cm<sup>3</sup>/sec, a value that we felt we could detect by coupling conventional flow-reactor techniques to our sensitive mass spectrometer molecular beam system. A simple flow tube equipped with a single oxygen source and IR emission diagnostic was assembled and used to search for the products of the related process:  $\text{O}_2(^1\Delta) + \text{O}_3 \rightarrow \text{labeled ozone}$ .

No exchange could be detected. Our detection limits were sufficient to place an upper limit of  $5 \times 10^{-16}$  cm<sup>3</sup>/sec on this rate coefficient, probably low enough to make the process insignificant in the atmosphere. A publication describing this work is in preparation.

3) We have begun assembly and testing of a three-color HeNe laser absorption experiment to determine cross sections accurately at three well-defined wavelengths near the peak of the Chappuis band. Preliminary results indicate that the precision of this method is very high; the knowledge of the ozone pressure will limit the absolute accuracy of these measurements to 1% or so. We plan to build on our previous work, using the ozone vapor pressure standard, to establish ozone pressures for the cross section measurements.

The solubility of HCl in materials forming Polar Stratospheric Clouds: In the past year, measurements of the solubility of hydrogen chloride in materials found in polar stratospheric cloud particles (PSCs) were carried out. Vapor phase HCl was allowed to equilibrate with frozen substrates at temperatures and pressures representative of the lower Antarctic stratosphere. The small solid substrates, comprising water ice, nitric acid trihydrate (NAT), and solid solutions of nitric acid and water, were analyzed for HCl content after saturation. Results show 1) a relatively high HCl solubility in NAT, 0.35 mol% at 200K and partial pressure of HCl at  $10^{-6}$  Torr; and 2) a low HCl solubility in pure ice, below 0.002 mol% under similar conditions, and 3) a strong dependence of HCl content on the amount of HNO<sub>3</sub> in the sample. Dissolved HCl increased about a factor of 3 for every tenfold increase of the HNO<sub>3</sub> content in ice.

Experiments were also conducted to determine the amount of HCl adsorbed on the surface of the ice samples. Results allowed an estimate of HCl surface covering which was found to be about 0.1 monolayer.

#### E. Journal Publications:

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2. "HCL/H<sub>2</sub>O Solid Phase Vapor Pressures and Solubility in Ice," D. Hanson and K. Mauersberger, *J. Chem. Phys.* **94**, 4700-4705 (1990).
3. "Near-Infrared Absorption Spectra of <sup>16</sup>O<sub>3</sub> and <sup>18</sup>O<sub>3</sub>: Adiabatic Energy of the <sup>1</sup>A<sub>2</sub> State?," S. Anderson, J. Morton and K. Mauersberger, *J. Chem. Phys.* **93**, 3826-3832 (1990).
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7. "HCL Solubility in Solid Mixtures of Nitric Acid and Ice: Implications for the Polar Stratosphere," J. Marti, K. Mauersberger and D. Hanson, *Geophys. Res. Lett.*, submitted, 1991.
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**BALLOON-BORNE LASER IN-SITU SENSOR (BLISS)  
AIRCRAFT LASER INFRARED ABSORPTION SPECTROMETER (ALIAS)**

**Principal Investigator:**

Dr. Christopher R. Webster

**Co-Investigator:**

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**ABSTRACT OF RESEARCH OBJECTIVES**

The Balloon-borne Laser In-Situ Sensor (BLISS) and the Aircraft Laser Infrared Absorption Spectrometer (ALIAS) programs have as their primary objective the collection of reliable data on the concentrations, distributions, and variabilities of the minor and trace species in the stratosphere. These powerful in-situ laser absorption spectrometers will support mid-latitude (UARS balloon correlative measurements, HSRP ER-2 flights) and high-latitude (AASE-II and ASHOM polar ozone ER-2 flights) campaigns over the next few years.

The BLISS balloon instrument, which has flown 8 times to date, uses tunable diode lasers in the 4 to 20- $\mu$ m wavelength region to measure the absorption due to selected species between the balloon gondola and a lowered retroreflector which defines a path of up to 1 km. The current measurement capability for a single flight includes: NO<sub>2</sub>, O<sub>3</sub>, HNO<sub>3</sub>, CH<sub>4</sub>, HCl, H<sub>2</sub>O, N<sub>2</sub>O, and CO<sub>2</sub>, with capability for more species. BLISS makes simultaneous, in-situ measurements of several gases with a 24-hr. capability for providing diurnal data as input for testing and constraining photochemical models.

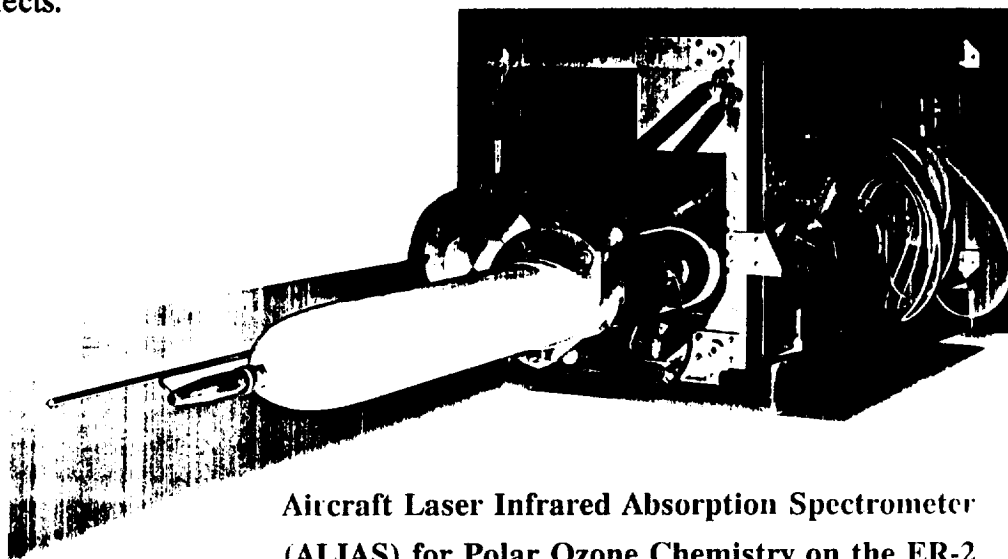
The ALIAS instrument is a very high resolution (0.0003 cm<sup>-1</sup>) scanning tunable diode laser spectrometer designed to make direct, simultaneous measurements of NO<sub>2</sub>, HNO<sub>3</sub>, HCl, CH<sub>4</sub>, and either O<sub>3</sub> or N<sub>2</sub>O [including vertical profiles of CH<sub>4</sub> and N<sub>2</sub>O] in the polar stratosphere at sub-part-per-billion level sensitivities over a 30 s integration time. For the Arctic AASE-II campaign, ALIAS will characterize and test the extent of denitrification by measurements of NO<sub>2</sub> and HNO<sub>3</sub>; of dehydration by measurements of H<sub>2</sub>O; of chlorine partitioning by measurements of HCl; of odd hydrogen partitioning by measurements of CH<sub>4</sub> and H<sub>2</sub>O; and of the atmospheric dynamics through measurements of the tracers CH<sub>4</sub> and N<sub>2</sub>O.

**SUMMARY OF PROGRESS AND RESULTS**

Since its highly successful balloon flight in Sept. 88, from which six journal publications have resulted, the BLISS instrument has not flown so that the JPL team

could focus on the build of the new ALIAS instrument for the ER-2. However, BLISS is currently being refurbished under the UARS Correlative Measurements Program for flights from the Fall 1992 on.

The Aircraft Laser Infrared Absorption Spectrometer (ALIAS) experiment for the ER-2 had successful test flights in Oct. 1991, demonstrating both the instrument concept and the engineering of the isokinetic sampling. Unique features include a sample inlet/throttle system designed to achieve near-isokinetic sampling in PSC events, an in-flight wavelength reference cell rack, a mechanical fringe-spoiler, a 4-laser/4-detector dewar with 24-hr. hold-time operating at a fixed temperature and in-flight fast correlation routines for spectral drift compensation prior to spectral addition. Since the test flights, ALIAS has been re-packaged over the last year for the upcoming AASE-II Arctic ozone campaign out of Alaska and Maine, beginning Fall 1992. ALIAS will measure  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{HCl}$ , and  $\text{HNO}_3$ . Recent tests in the laboratory of the instrument response to injected amounts of  $\text{HCl}$  have characterized and verified its ability to reliably measure stratospheric acids with only minimal wall sticking effects.



Aircraft Laser Infrared Absorption Spectrometer  
(ALIAS) for Polar Ozone Chemistry on the ER-2

## JOURNAL PUBLICATIONS

1. "Theoretical Interpretation of  $\text{N}_2\text{O}$  Measurements", R. Toumi, J.A. Pyle, C.R. Webster, and R.D. May, *Geophys. Res. Letters*, **18**, 1213-1216, 1991.
2. "The BLISS Measurements of  $\text{NO}_2$ : Some New Insights", D.J. Lary, J.A. Pyle, C.R. Webster, and R.D. May, submitted to *Geophys. Res. Letters*, 1991.
3. "In Situ Stratospheric Measurements of  $\text{CH}_4$ ,  $^{13}\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and  $\text{OC}^{18}\text{O}$  using the BLISS Tunable Diode Laser Spectrometer", C. R. Webster and R. D. May, submitted to *Geophys. Res. Letters*, 1991.

## **A. Balloon-Borne and Aircraft-Borne, In Situ Measurements of Stratospheric Free Radicals**

**B. James G. Anderson, Harvard University**

**C. Abstract** Free radicals from the chlorine, bromine, hydrogen, oxygen, and nitrogen families constitute the catalytic chain sustaining species which dictate chemical transformation rates in the stratosphere and troposphere. This research is directed toward *in situ* detection of OH, HO<sub>2</sub>, Cl, ClO, BrO, O<sub>3</sub>, and H<sub>2</sub>O from balloons and from the ER-2 aircraft. The scope of the work embraces balloon and aircraft field programs, instrument development, data analysis, and interpretation based on photochemical calculations. Isolating and quantifying ozone destruction mechanisms in the midlatitude and polar stratospheres is the abiding objective.

## **D. Summary of Progress and Results**

1. *Antarctic ozone loss.* The Antarctic continues to serve as a crucial laboratory for diagnosis of processes directly implicated in the observed O<sub>3</sub> loss over the polar regions. Specifically results from the AAOE mission have been used to establish three lines of evidence defining a link between CFC release and O<sub>3</sub> loss within the Antarctic vortex: (i) observed containment in the vortex of ClO concentrations two orders of magnitude greater than normal levels; (ii) *in situ* observations obtained during ten high-altitude aircraft flights into the vortex as the O<sub>3</sub> hole was forming that show a decrease in O<sub>3</sub> concentrations as ClO concentrations increased; and (iii) a comparison between observed ozone loss rates and those predicted with the use of absolute concentrations of ClO and BrO, the rate-limiting radicals in an array of proposed catalytic cycles. Recent advances in our understanding of the kinetics, photochemistry, and structural details of key intermediates in these catalytic cycles as well as an improved absolute calibration for ClO and BrO concentrations at the temperatures and pressures encountered in the lower Antarctic stratosphere have been essential for defining the link.

2. *Perturbed chemistry within the Arctic vortex.* At present the nature of the Arctic polar stratosphere is observed to be similar in many respects to that of the Antarctic polar stratosphere, where an O<sub>3</sub> hole has been identified. Most of the available chlorine (HCl and ClONO<sub>2</sub>) was converted by reactions on polar stratospheric clouds to reactive ClO and Cl<sub>2</sub>O<sub>2</sub> throughout the Arctic polar vortex before midwinter. Reactive nitrogen was converted to HNO<sub>3</sub>, and some, with spatial inhomogeneity, fell out of the stratosphere. These chemical changes ensured characteristic O<sub>3</sub> losses of 10 to 15% at altitudes inside the polar vortex where polar stratospheric clouds had occurred. These local losses can translate into 5 to 8% losses in the vertical column abundance of O<sub>3</sub>. As the amount of stratospheric chlorine inevitably increases by 50% over the next two decades, O<sub>3</sub> losses recognizable as an O<sub>3</sub> hole may well appear.

In the next decade the possibility of substantial O<sub>3</sub> loss in the Arctic polar vortex will increase, however, because stratospheric chlorine will inevitably increase from ~3200 to ~5000 pptv in the next two decades. Bromine may increase as well. Even total international compliance with a recent agreement to stop the production and use of most chlorofluorocarbons and Halons by 2000 cannot prevent these increases. As chlorine increases, the increased rate of chlorine-induced O<sub>3</sub> destruction will cause more O<sub>3</sub> to be lost during the lifetime of the polar vortex. Also, the effectiveness of reactive nitrogen for slowing halogen-induced O<sub>3</sub> loss will be diminished as the abundance of chlorine approaches that of reactive nitrogen. As a result, the destruction of O<sub>3</sub> by chlorine will increase by a factor of 1.5 to 2, and losses in the vertical column abundances inside the Arctic polar vortex may become 10 to 20% by the year 2010. These estimates are based on the assumptions that climate will not change radically and that we can estimate the future increases in other stratospheric gases by projecting the current rates of change. If climate does change in response to the increases in greenhouse gases such as CO<sub>2</sub> and CH<sub>4</sub>, then the lower stratosphere would be expected to cool. Lower temperatures will lead to more frequent and widespread PSCs, which ultimately will lead to even greater O<sub>3</sub> destruction. Thus, an Arctic O<sub>3</sub> hole, smaller and less intense than the Antarctic O<sub>3</sub> hole, is possible in the near future.

The potential for substantial O<sub>3</sub> depletion in the Arctic polar stratosphere no longer depends simply on atmospheric dynamics. It also increasingly depends on the international policies that govern the use of long-lived chlorine and bromine compounds and that moderate the anthropogenic effects on climate.

3. *Midlatitude ClO and heterogeneous processes.* The decline in stratospheric O<sub>3</sub> at northern midlatitudes in wintertime may be caused by chlorine photochemistry that has been enhanced by heterogeneous reactions. The possibility that heterogeneous reactions of N<sub>2</sub>O<sub>5</sub> on background aerosols is the cause of this decadal O<sub>3</sub> decline can be addressed by comparing ClO measurements in the lower stratosphere with results from a

two-dimensional model. Measurements of ClO and O<sub>3</sub> on two flights covering 21°N to 61°N latitude and 400 to 525 K potential temperature show that ClO increases with latitude, as predicted by the model containing heterogeneous chemistry on background aerosols, but the slope of the increase is greater than predicted. Further, midlatitude ClO is greater in winter than summer by a factor of five. This seasonal variation is greater than that predicted by the model. On the other hand, the observed latitudinal and seasonal variations of ClO disagree strongly with the results of two-dimensional models that contain only gas-phase chemistry. Missing or misunderstood photochemistry, or heterogeneous chemistry associated with the Arctic polar vortex may be contributing to the observed ClO signal.

4. *Development of lightweight instrument for ClO, BrO, O<sub>3</sub>, NO, NO<sub>y</sub>, P, and T for small balloons and the Perseus unmanned aircraft.* A critical constraint on our ability to quantify O<sub>3</sub> loss processes is lack of data between 20 and 30 km at both poles. We have thus developed lightweight instrumentation to detect key radicals and nitrogen reservoir species from unmanned aircraft and balloons. The prototype instrument was flown in February 1991 from Fort Sumner, NM. Performance of the system was excellent. Three of these instruments will be launched from Sondrestromme, Greenland as part of the AASE II mission to map ClO, BrO, O<sub>3</sub>, NO, NO<sub>y</sub>, P, and T to altitudes of 30 km. That instrument will then fly on the prototype Perseus aircraft in 1992-93.

5. *Development of solid state laser system for detection of OH and HO<sub>2</sub> from the ER-2.* A major shortcoming of the ER-2 instrument complement has been the absence of OH and HO<sub>2</sub> observations. The scientific requirements of the NASA HSRP program dictate the inclusion of HO<sub>x</sub> radical detection in the instrument array. We have thus undertaken the development of an LIF system using recently developed diode pumped YLF lasers to achieve performance figures exceeding our balloon borne copper vapor laser system by more than an order of magnitude.

6. *Preparation for AASE II.* We have accepted responsibility for the mission scientist position in the upcoming Airborne Arctic Stratospheric Experiment II which will address two questions: (a) Will significant ozone erosion occur within the Arctic vortex as chlorine loading approaches 5 ppbv? (b) What is the process responsible for O<sub>3</sub> erosion over the past decade observed by satellite over the mid-high latitude northern hemisphere?

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1. Anderson, J. G., W. H. Brune, and D. W. Toohey, "Free radicals within the antarctic vortex: The role of CFCs in antarctic ozone loss," *Science* **251**, 39-46, 1991.
2. Brune, W. H., D. W. Toohey, J. G. Anderson, D. W. Fahey, S. R. Kawa, R. L. Jones, D. S. McKenna, and L. R. Poole, "The potential for ozone depletion in the arctic polar stratosphere," *Science* **252**, 1260-1266, 1991.
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6. Brune, W. H., D. W. Toohey, S. A. Lloyd, and J. G. Anderson, "The sunrise and sunset variation of ClO in the lower stratosphere," *Geophys. Res. Lett.* **17**, 509-512, 1990.
7. Wennberg, P. O., R. M. Stimpfle, E. M. Weinstock, A. E. Dessler, S. A. Lloyd, L. B. Lapson, J. J. Schwab, and J. G. Anderson, "Simultaneous, in situ measurements of OH, HO<sub>2</sub>, O<sub>3</sub>, and H<sub>2</sub>O: A test of modeled stratospheric HO<sub>x</sub> chemistry," *Geophys. Res. Lett.* **17**, 1909-1912, 1990.
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11. Weinstock, E. M., J. J. Schwab, J. B. Nee, M. J. Schwab, and J. G. Anderson, "A cryogenically-cooled photofragment fluorescence instrument for measuring stratospheric water vapor," *Rev. Scientific Instr.* **61**, 1413-1432, 1990.

## Measurements of Nitric Oxide and Total Odd Nitrogen in the Stratosphere

A.J. Weinheimer, J.G. Walega, F.E. Grahek, B.A. Ridley

National Center for Atmospheric Research, Boulder, CO 80307 \*

### Objectives

A balloon instrument has been developed for the measurement of NO and is being modified for the measurement of NO<sub>y</sub>. The NO configuration was designed for collaborative flights on the Harvard large gondola. The emphasis is now shifting toward NO<sub>y</sub> measurements in conjunction with collaborators on the JPL gondola, though the capability for NO measurements is being maintained. Collaborative flights with JPL are being planned as part of the UARS correlative program in 1992.

### Progress

In 1990, improvements were made to the NO instrument and calibrations were performed in anticipation of a flight of the Harvard gondola from Palestine in the summer. An inlet with better flow measuring capability was designed and constructed using improved temperature control. A new data acquisition system was added that will improve reliability and provide the additional capacity required for the NO<sub>y</sub> measurement. The NO instrument attained flight readiness at Palestine in a timely fashion; however, problems with other instrumentation and with weather conditions precluded a flight.

In 1991, the focus has been on implementing the inlet changes that are required for the NO<sub>y</sub> measurement and on planning and coordination with JPL to insure compatibility and to arrange a flight schedule. A new inlet valve has been designed and

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\* The National Center for Atmospheric Research is sponsored by the National Science Foundation



constructed, and work is proceeding on incorporating this new valve as well as the already tested NO<sub>y</sub> converter into a new inlet structure.

In addition in 1991, we have recently committed to fly on the NASA DC-8 as part of AASE II. This has led to some delays in the balloon project, in order to accommodate the timing of the DC-8 missions, but this is consistent with the priorities of NASA and is done with their concurrence. Most importantly, we should be ready to participate in the UARS correlative flights.

## **Publications**

Weinheimer, A. J., and B. A. Ridley, A cautionary note on the use of some mass flow controllers, *J. Geophys. Res.*, **95**, 9817-9821, 1990.



**B. BALLOON-BORNE REMOTE MEASUREMENTS**

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**FBI** *27* **LABORATORY**



TITLE OF RESEARCH TASK: Infrared Measurements of Atmospheric Constituents

INVESTIGATORS: David G. Murcray, Physics Department, University of Denver  
Frank J. Murcray, Physics Department, University of Denver  
Aaron Goldman, Physics Department, University of Denver  
Curtis P. Rinsland, NASA Langley Research Center  
C. Camy-Peyret, Lab. de Phys. Moléculaire et Atmosphérique  
J.M. Flaud, Lab. de Phys. Moléculaire et Atmosphérique

ABSTRACT OF RESEARCH OBJECTIVES:

The objective of this program is to obtain data concerning the concentration versus altitude of various chemical constituents pertinent to the photochemistry of the stratospheric ozone layer. Data are obtained using balloon-borne instruments to measure the atmospheric transmission and emission in the mid infrared. In addition to obtaining constituent profile information, the spectral data obtained are also used to identify absorption or emission features which may interfere with the retrieval of constituent data from satellite instruments that use lower spectral resolution.

SUMMARY OF PROGRESS AND RESULTS:

The primary instrumentation used on this program is a very high resolution ( $0.002\text{ cm}^{-1}$ ) interferometer system. This system is interfaced with a solar tracking system so that high resolution solar spectra can be obtained while the unit is flown on a balloon. In order to enhance the sensitivity of the system for the detection and measurement of trace constituents, the flights are performed so as to obtain data during solar occultation. The system has been flown twice during the period covered by this report. The first flight was performed from Palestine, Texas on June 4, 1990. The second flight was performed on June 17, 1991. Both flights were successful, and solar spectral data were obtained during sunset on the June 4, 1990 flight and during sunrise on the June 17, 1991 flight. The spectral bandpass for the June 17 flight was from  $1050\text{ cm}^{-1}$  to  $1940\text{ cm}^{-1}$  which includes absorption features due to  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{H}_2\text{O}$  and  $\text{O}_3$ . The June 4, 1990 covered much of the same spectral region, however the data were obtained during sunset. The two flights should yield data concerning the diurnal variability of these compounds. Spectral resolution achieved on both flights was  $0.0025\text{ cm}^{-1}$  apodized.

Analysis of the data obtained on these and earlier flights has been continuing during this period. The spectra obtained at this very high resolution contain many features which have not previously been observed. Identification of these features is time consuming since the laboratory data for some of the compounds is not available at the resolution required for positive identification. In many cases it is necessary to use the balloon data to update the theoretical analysis of the compound responsible for the absorption in order to validate the identification. A number of the publications during

this period are the result of this type of analysis. Publications on this program during this period also include a number of publications resulting from the flights made during the BIC campaign.

In addition to the flights made with the balloon-borne solar spectrometer instrumentation, three flights have also been made with small atmospheric emission sondes designed to obtain  $\text{HNO}_3$  profiles by measuring the change in the  $11\mu\text{m}$  atmospheric emission with altitude. The balloon flights were made January 17 and 30, 1990 from Kiruna, Sweden and October 26, 1990 from Aire sur l'Adour, France. All flights went very well and data were obtained on all three flights. The January flight was particularly interesting since it showed a layer of depleted  $\text{HNO}_3$  in the region where polar stratospheric clouds were observed.

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- Goldman, A., F.J. Murcray, C.P. Rinsland, R. D. Blatherwick, F.H. Murcray and D.G. Murcray, "Analysis of Atmospheric Trace Constituents from High Resolution Infrared Balloon-Borne and Ground-Based Solar Absorption Spectra," SPIE 1991, April 1-5, Orlando, Florida.
- Farmer, C.B., B. Carli, A. Bonetti, M. Carlotti, B.M. Dinelli, H. Fast, N. Louisnard, C. Alamichel, W. Mankin, M. Coffey, I.G. Nolt, D.G. Murcray, A. Goldman, G. Stokes, D. Johnson, W. Traub, K. Chance, R. Zander, L. Delbuiolle and G. Roland, "Balloon Intercomparison Campaigns: Result of Remote Sensing Measurements of  $\text{HCl}$ ," J. Atmos. Chem., 10, 237-272, 1990.
- Murcray, D.G., A. Goldman, J. Kusters, R. Zander, W. Evans, N. Louisnard, C. Alamichel, M. Bangham, S. Pollitt, B. Carli, B. Dinelli, S. Piccioli, A. Volboni, W. Traub and K. Chance, "Intercomparison of Stratospheric Water Vapor Profiles Obtained During the Balloon Intercomparison Campaign," J. Atom. Chem., 10, 159-179, 1990.
- Rinsland, C.P., A. Goldman, F.J. Murcray, R.D. Blatherwick, J.J. Kusters, D.G. Murcray, N.D. Sze, S.T. Massie, "Long-Term Trends in the Concentrations of  $\text{SF}_6$ ,  $\text{CHClF}_2$ , and  $\text{COF}_2$  in the Lower Stratosphere from Analysis of High-Resolution Infrared Solar Occultation Spectra," J. Geophys. Res., 95, 16477-16490, 1990.
- Murcray, F.J., J.J. Kusters, R.D. Blatherwick, J. Olson and D.G. Murcray, "High Resolution Solar Spectrometer System for Measuring Atmospheric Constituents," Appl. Opt., 29, 1520-1525, 1990.
- Kondo, T., P. Amedieu, W. Matthews, D. Fahey, D. Murcray, D. Hoffman, P. Johnston, Y. Iwasaka, A. Iwata and W. Sheldon, "Balloon Borne Measurements of Total Reactive Nitrogen, Nitric Acid and Aerosols in the Cold Arctic Stratosphere," Geophys. Res. Lett., 17, 437-440, 1990.

## **Measurement of HO<sub>2</sub> and Other Trace Species in the Stratosphere Using a High Resolution Far-Infrared Spectrometer**

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Harvard-Smithsonian Center for Astrophysics, Cambridge, MA  
Steven C. Wofsy

Center for Earth and Planetary Physics, Harvard University, Cambridge, MA

### **Abstract of Research Objectives**

Our research strategy is to measure the abundances of about a score of stratospheric species as functions of altitude and time, and to compare these results to theoretical calculations in order to confirm or revise the underlying models. Our observational technique is to use a remote-sensing far-infrared Fourier-transform spectrometer (FIRS-2) mounted on a balloon platform at about 37 km or, recently, on a DC-8 aircraft platform at 12 km. The spectrometer has an unapodized resolution of  $0.004\text{ cm}^{-1}$ , and operates simultaneously in the far-infrared ( $70\text{--}220\text{ cm}^{-1}$ ) and mid-infrared ( $350\text{--}700\text{ cm}^{-1}$ ) regions. We measure the stratospheric thermal emission spectrum, so data is acquired continuously day and night.

### **Summary of Progress and Results**

We made the first detection of stratospheric HO<sub>2</sub> in the far-infrared. Prior to our work, earlier measurements with some techniques indicated mixing ratios greatly exceeding theoretical predictions. Using 5 of the strongest lines of HO<sub>2</sub> in our balloon-flight spectra, we were able to measure day-time as well as night-time profiles which are in generally good agreement with model predictions.

We made the first unequivocal measurement of stratospheric H<sub>2</sub>O<sub>2</sub>. Previously, a number of upper-limit values had been published for H<sub>2</sub>O<sub>2</sub>, including some of our own. Comparison of the current results with a theoretical model indicates generally good agreement in the neighborhood of 30 km altitude, but about a factor of 2 measured excess about one scale height above as well as below this level.

Work in progress on OH shows that the OH signals measured at balloon altitudes are in apparently good agreement with those expected from photochemical modeling. For example, we have measured the power in the OH line at  $83.87\text{ cm}^{-1}$  at intervals from noon to midnight, and have found a close match with theory.

Further work in progress includes measurement of isotopic water and ozone. Our results to date suggest that there is no significant enhancement of either oxygen 17 or 18, in water or ozone, at about the 10 percent level. On the other hand, heavy water (HDO) is depleted to roughly half its sea level relative abundance. Also, a substantial effort was made to extract accurate temperature and pressure values from our spectra, allowing us to independently derive a stratospheric temperature profile, and also to calibrate our elevation pointing angles. The resulting accuracies are about 2 K in temperature and 0.05 degree in angle.

During this period we began preparations for two major measurement campaigns. First, as Correlative Investigators for the Upper Atmosphere Research Satellite

(UARS), we are working to greatly reduce our data-analysis time, so that complete profile information will be available roughly a month after each of our upcoming UARS correlative balloon flights. Second, as Airborne Arctic Stratospheric Expedition investigators during the 1991-92 campaign, we will fly the FIRS-2 on the NASA DC-8 on monthly runs over the Arctic winter vortex. New, and even faster, data analysis methods are being developed for this expedition.

## Publications

- Stratospheric Hydroperoxyl Measurements, W. A. Traub, D. G. Johnson, and K. V. Chance, *Science* **247**, 446-449, 1990.
- Intercomparison of Stratospheric Water Vapor Profiles Obtained During the Balloon Intercomparison Campaign, D. G. Murcray, A. Goldman, J. Kusters, R. Zander, W. Evans, N. Louisnard, C. Alamichel, M. Bangham, S. Pollitt, B. Carli, B. Dinelli, S. Piccioli, A. Volboni, W. A. Traub, and K. Chance, *Journal of Atmospheric Chemistry* **10**, 159-179, 1990.
- Ozone Measurements During the Balloon Intercomparison Campaign, D. Robbins, J. Waters, P. Zimmerman, R. Jarnot, J. Hardy, H. Pickett, S. Pollitt, W. A. Traub, K. Chance, N. Louisnard, W. Evans, and J. Kerr, *Journal of Atmospheric Chemistry* **10**, 181-218, 1990.
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- Balloon Intercomparison Campaigns: Results of Remote Sensing Measurements of HCl, C. B. Farmer, B. Carli, A. Bonetti, M. Carlotti, B. M. Dinelli, H. Fast, W. F. J. Evans, N. Louisnard, C. Alamichel, W. Mankin, M. Coffey, I. G. Nolt, D. G. Murcray, A. Goldman, G. M. Stokes, D. W. Johnson, W. A. Traub, K. V. Chance, R. Zander, and L. Delbouille, *Journal of Atmospheric Chemistry* **10**, 237-272, 1990.
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- Stratospheric Spectroscopy with the Far Infrared Spectrometer (FIRS-2): Overview and Recent Results, W. A. Traub, K. V. Chance, D. G. Johnson, and K. W. Jucks, *Proc. SPIE*, **1491**, in press, 1991.
- Measurement of the Stratospheric Hydrogen Peroxide Concentration Profile Using Far-Infrared Thermal Emission Spectroscopy, K. V. Chance, D. G. Johnson, W. A. Traub, and K. W. Jucks, *Geophysical Research Letters* **18**, 1003-1006, 1991.



## **Far-Infrared Trace Gas Measurements**

### **Principal Investigator:**

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### **Abstract of Research Objectives:**

The objective of this program is to continue a long-term collaborative United States/Italian effort for the study of trace-gas compositions of the stratosphere. The effort combines an Italian-developed high-resolution Fourier transform (FT) spectrometer with United States-based sensor, gondola, and analysis support. These balloon-based measurements of the far-infrared limb emission are intended to provide validation and complementary data for the upcoming Upper Atmospheric Research Satellite (UARS) mission. Priority species for measurement are H<sub>2</sub>O, OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, HOCl, HCl, HF, HBr, HDO, O<sub>3</sub>, and isotopes of O<sub>3</sub>.

### **Summary of Progress and Results (Fiscal Year 1990-1991):**

The major effort has been to refurbish and upgrade the Italian Fourier transform spectrometer to achieve higher spectral resolution, and more precise vertical

pointing in preparation for a series of UARS validation support flights in 1992-1993. This project is an officially-approved NASA/Italian Space Agency (ASI) Cooperative Project. An engineering flight test of the system (Infrared Balloon Experiment, (IBEX)) was made from Ft. Sumner, New Mexico, in October 1990. The flight demonstrated successful operation of the improved vertical pointing system and the higher resolution ( $0.002\text{ cm}^{-1}$ ) mirror drive system of the interferometer. However, an electronic problem prevented full science data recovery from the engineering flight. The payload is presently being refurbished for UARS validation flights in 1992 and 1993.

Data analyses were made of previous 1983 flight data for measurements of  $\text{HO}_2$ ,  $\text{H}_2\text{O}_2$ , and OH in the stratosphere. In addition, assistance was provided to a program of laboratory spectroscopy measurements. This work is a collaboration with the National Institute for Standards and Technology, the University of Oregon, and the Smithsonian Astronomical Observatory. Principal results of this work are accurate pressure-broadening coefficients for retrievals of stratospheric OH and HCl from far-infrared measurements, and line center frequency measurement for more accurate molecular constants of  $\text{HO}_2$ .

#### **Journal Publications (1990-1991):**

1. "Pressure Broadening of the  $118.455\text{ cm}^{-1}$  Rotational Line of OH by  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{O}_2$ ," by K. V. Chance, D. A. Jennings, K. M. Evenson, M. D. Vanek, I. G. Nolt, J. V. Radostitz, and K. Park; *J. Mol. Spect.* **146**, 375-380, 1991.
2. "Pressure Broadening of the 2.5 THz HCl Rotational Line by  $\text{N}_2$  and  $\text{O}_2$ ," by K. Park, K. V. Chance, I. G. Nolt, J. V. Radostitz, M. D. Vanek, D. A. Jennings, and K. M. Evenson, *J. Mol. Spect.* **147**, 521-525, 1991.
3. "Spectroscopic Measurements of  $\text{HO}_2$ ,  $\text{H}_2\text{O}_2$ , and OH in the Stratosphere," by J. Park and B. Carli, *J. Geophys. Res.* (in press).

## Measurement of the Solar UV Flux and Its Variability

Principle Investigator: James E. Mentall  
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### ABSTRACT

Measurements are made of the Sun's ultraviolet spectral irradiance between 150 and 350 nm in order to obtain a complete set of measurements over a complete solar cycle. Observations are made using three rocket-born spectrometers to cover the entire spectral region. Calibration of the spectrometers are performed using the NIST Electron Synchrotron Storage Ring (SURF) with NIST calibrated standard lamps being used in wavelength regions where SURF does not have sufficient intensity to obtain the required accuracy. Solar spectra are obtained with a nominal absolute error of  $\pm 5\%$  and repeatability to within  $\pm 2\%$ . Measurements are made once per year with satellite data being used to determine the relative variability between flights. Comparison of these rocket measurements with other measurements provides insight into the absolute accuracy of solar flux measurements and the drift in the satellite instruments.

### SUMMARY OF PROGRESS AND RESULTS

Measurements have been made from 1978 to 1990 covering 1 1/2 solar cycles. Results from these flights have shown that the solar variability at 150 nm is only on the order of 10%. These measurements also show the beginning in 1982, the sensitivity of the Nibus 7 SBUV instrument started to decrease significantly below 200 nm. The measurement phase of this program has been completed and the current effort is to correct the calibration and flight data for small known errors. The calibration data has been reprocessed and work is now in progress on the flight data. Because the experimental errors above 200 nm are larger than the solar variability in this wavelength region, the final data set will be a absolute solar flux from 200 to 350 nm with an absolute accuracy to within  $\pm 5\%$ .

## Biennial Research Summary

A. Title: Stratospheric Fourier Spectroscopy

B. Principal Investigator: Geoffrey C. Toon  
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### C. Abstract of Research Objectives:

The MkIV interferometer is a high resolution Fourier transform infrared spectrometer purpose-built at the Jet Propulsion Laboratory to measure solar absorption spectra from ground-based, airborne and balloon-borne platforms. From the absorptions in such spectra, the abundances of more than 20 different atmospheric gases, many of which play important roles in determining the global distribution of ozone, can be measured simultaneously and with good precision. These data can then be used to validate computer models of the atmospheric transport and photochemistry over a range of different geographic locations and seasons.

### D. Summary of Progress and Results during 1990 and 1991:

Some 2000 spectra, measured from the NASA DC-8 aircraft during the Airborne Arctic Stratosphere Experiment (AASE) of January and February 1989, have been analyzed to determine the vertical column contents of  $\text{CO}_2$ ,  $\text{HCN}$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{OCS}$ ,  $\text{CHF}_2\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ ,  $\text{O}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ ,  $\text{ClNO}_3$ ,  $\text{HOCl}$ ,  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{H}_2\text{O}$  and  $\text{HDO}$ . The results confirmed that inside the polar vortex subsidence had occurred and that heterogeneous reactions were destroying  $\text{HCl}$  and  $\text{ClNO}_3$  while enhancing  $\text{HNO}_3$ .

In Oct 1989, Sept 1990 and May 1991 successful balloon flights were performed from Ft. Sumner, New Mexico. Sunrise transitions were observed on each flight from float altitudes of 36-39 km, and during the latest flight a sunrise was also obtained. Each spectrum, measured every 105 s, covers the entire 650-5400  $\text{cm}^{-1}$  spectral region at 0.01  $\text{cm}^{-1}$  resolution. Analysis of these spectra is in progress and some exciting results are anticipated. In addition to the gases named above, we will retrieve simultaneous vertical profiles of  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_4$ ,  $\text{COF}_2$ ,  $\text{CF}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{D}$  and various ozone isotopes from these spectra.

In addition to these activities ground-based observations continue to be performed. A ceostat was installed in the South wall of the fourth floor of JPL building 183 to allow solar observations to be made from inside. This has enabled us, following the eruption of Mt. Pinatubo, to make observations thrice weekly with minimal impact on our other activities, and will allow us to make ground-based observations during UARS overpasses.

Since the May 1991 balloon flight the main thrust of our activities has been the preparation of the MkIV instrument for the upcoming AASE II campaign. To make room for additional experiments on board the DC-8 aircraft, the MkIV instrument has been rotated through 90° and moved forward. In doing this we have redesigned the mounting structure to allow the suntracker to be translated in the fore-aft direction during flight to allow a wider azimuthal field of view through the window.

#### E. Journal Publications in 1990 and 1991.

G.C.Toon, The JPL MkIV Interferometer, submitted to Optics and Photonics News (1991)

G.C.Toon, C.B.Farmer, P.W.Schaper, L.L.Lowes and R.H.Norton, Composition measurements of the 1898 Arctic winter stratosphere by airborne infrared solar absorption spectrometry, submitted to J.Geophys.Res.(1991)

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S.C.Wofsy, J.H.Yatteau, R.J.Salawitch, M.B.McElroy, G.C.Toon, W.G.Mankin, and M.T.Coffey, Heterogeneous conversion of COF<sub>2</sub> to HF in polar stratospheric clouds, Geophys.Res.Lett., 17, 461-464, 1990

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J.M.Rodriguez, M.K.W.Ko, N.D.Sze, S.D.Pierce, J.G.Anderson, D.W.Fahey, K.Kelly, C.B.Farmer, G.C.Toon, M.T.Coffey, L.E.Heidt, W.G.Mankin, K.R.Chan, W.L.Starr, J.F.Vedder, and M.P.McCormick, Nitrogen and Chlorine Species in the Spring Antarctic Stratosphere: Comparison of models with airborne Antarctic Ozone Experiment observations, J.Geophys.Res., 94, 16683-16703, 1989

C.P.Rinsland, G.C.Toon, C.B.Farmer, R.H.Norton and J.S.Namkung, Stratospheric N<sub>2</sub>O<sub>5</sub> profiles at sunrise and sunset from further analysis of the ATMOS Spacelab 3 solar spectra, J.Geophys.Res., 94, 18341-18349, 1989

**A. Title of Research Task:** Millimeter and Submillimeterwave Radiometry.

**B. Investigators:**

Dr. R.A. Stachnik, Jet Propulsion Laboratory

Dr. J.W. Waters, Jet Propulsion Laboratory

**C. Abstract of Research Objectives:** The objective of this program is measure abundance and variability of stratospheric trace constituents which influence stratospheric ozone using balloon and aircraft-borne millimeter and sub-millimeter wave spectrometers. The present instrumentation simultaneously measures  $O_3$  and ClO, a key indicator of Cl-catalyzed  $O_3$  destruction, HCl, and  $HO_2$ . Additional capability for  $HNO_3$  and  $N_2O$  measurements is under development. This program also provides a background for development of satellite instrumentation which can yield measurements on a global scale. Technology developed by this program has been used in the Microwave Limb Sounder (MLS) instrument on Upper Atmosphere Research Satellite (UARS) and will be essential to the development of the proposed MLS instrument on the Earth Observing System (EOS) platform.

**D. Summary of Progress and Results:**

1. The Balloon Microwave Limb Sounder (BMLS) instrument, a 205 GHz radiometer measuring  $O_3$  and ClO with spectral coverage and resolution identical to that of the UARS MLS instrument, was successfully flown from the National Scientific Balloon Facility (NSBF) site at Ft. Sumner NM in September 1989 and June 1990 on the JPL multi-instrument gondola. These flights were made jointly with the far infrared spectrometer of the Smithsonian Astrophysical Observatory, and the JPL far infrared limb observer and the  $O_3$  photometer instrument.
2. The JPL Submillimeterwave Limb Sounder (SLS) instrument, a 600 GHz radiometer, was successfully launched for its first flight on a high altitude balloon from Daggett, CA on 9 April 1991. Figure 1 shows a sample of the atmospheric spectra recorded during this flight. Figure 2 are abundance profiles for  $O_3$ , ClO and HCl inferred from these measurements. The second flight of this instrument is planned for September 1991.
3. A series of balloon flights of the SLS and BMLS instruments is planned under the UARS Correlative Measurements program during 1992-93 from mid-latitudes sites, Antarctica and the tropics.

**E. Journal Publications:** none (manuscripts are in preparation).

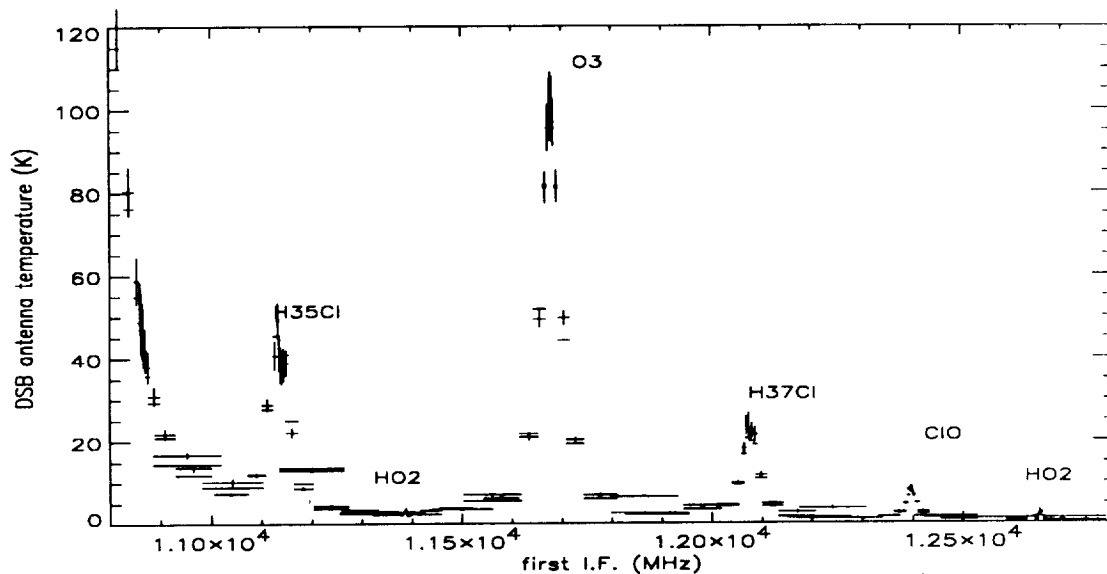


Figure 1: Emission spectrum measured (vertical and horizontal extents) by the SLS instrument and calculated spectrum (horizontal extents only) using retrieved species vmr. Balloon altitude 38 km; 35 km tangent height view.

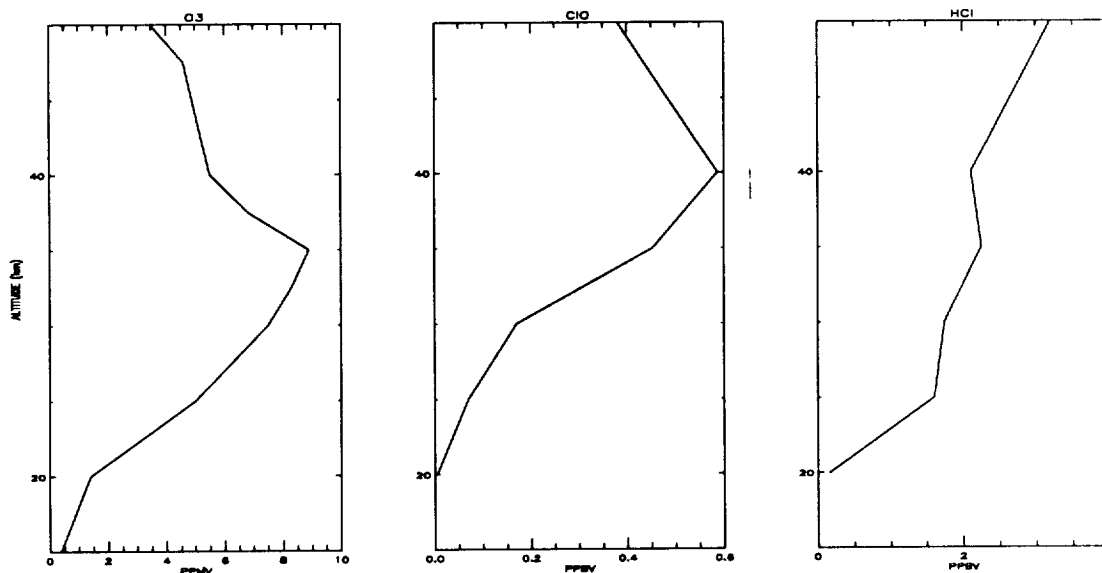


Figure 2: Retrieved volume mixing ratios for  $O_3$ ,  $ClO$  and  $HCl(H^{35}Cl + H^{37}Cl)$  from mid-day measurements by the SLS instrument on 9 April 1991.

**A. Title:** Far Infrared Balloon Radiometer for OH

**B. Investigators:** Herbert M. Pickett and Dean B. Peterson  
Jet Propulsion Laboratory  
California Institute of Technology  
Pasadena, CA 91109

**C. Objectives:**

A stratospheric hydroxyl radical (OH) radiometer for balloon observations in the far infrared region of the spectrum is being developed. The instrument uses three Fabry-Perot resonators to resolve stratospheric limb emission of OH at  $101\text{ cm}^{-1}$  ( $99\text{ }\mu\text{m}$  wavelength). The spectral resolution of  $0.0017\text{ cm}^{-1}$  is used to match the width of the stratospheric OH emission. The instrument is compact and designed to fly jointly with other balloon measurements. The goal of this task is to determine OH concentrations from 25-45 km with better than 10% accuracy.

**D. Progress and Results:**

The first scientific balloon flight was made on May 15, 1989. OH radical emission from two different lines was definitely identified during the day and decayed as expected after sunset. Features due to HDO, vibrationally excited  $\text{H}_2\text{O}$ , and  $\text{O}_3$  were also identified. Since that time, the instrument has been part of four additional stratospheric measurement campaigns. Results from the flight in April 1991 is shown in the figure. These data were obtained in mid-afternoon and at night with 32 sec of integration time per point. In addition to this data, altitude and time resolved concentration measurements of OH were made during sunset to test the temporal behavior of OH production and loss chemistry.

Since the first flight, significant improvements in the performance of the instrument have been made. The signal-to-noise performance of the detector system is now at least a factor of 5 better, meaning that noise performance requiring 6 hours of integration on the first flights can now be obtained in less than 15 minutes. In addition we have made significant strides in improving the mechanical robustness and stability of the main Fabry-Perot etalon, which must be scanned with  $0.1\text{ }\mu\text{m}$  accuracy in position. Finally, we have made important improvements in the calibration of the instrument, and are continuing to work on the spectral constants of water and ozone to assure that these species are adequately modeled in the spectrum.

**E. Publications:**

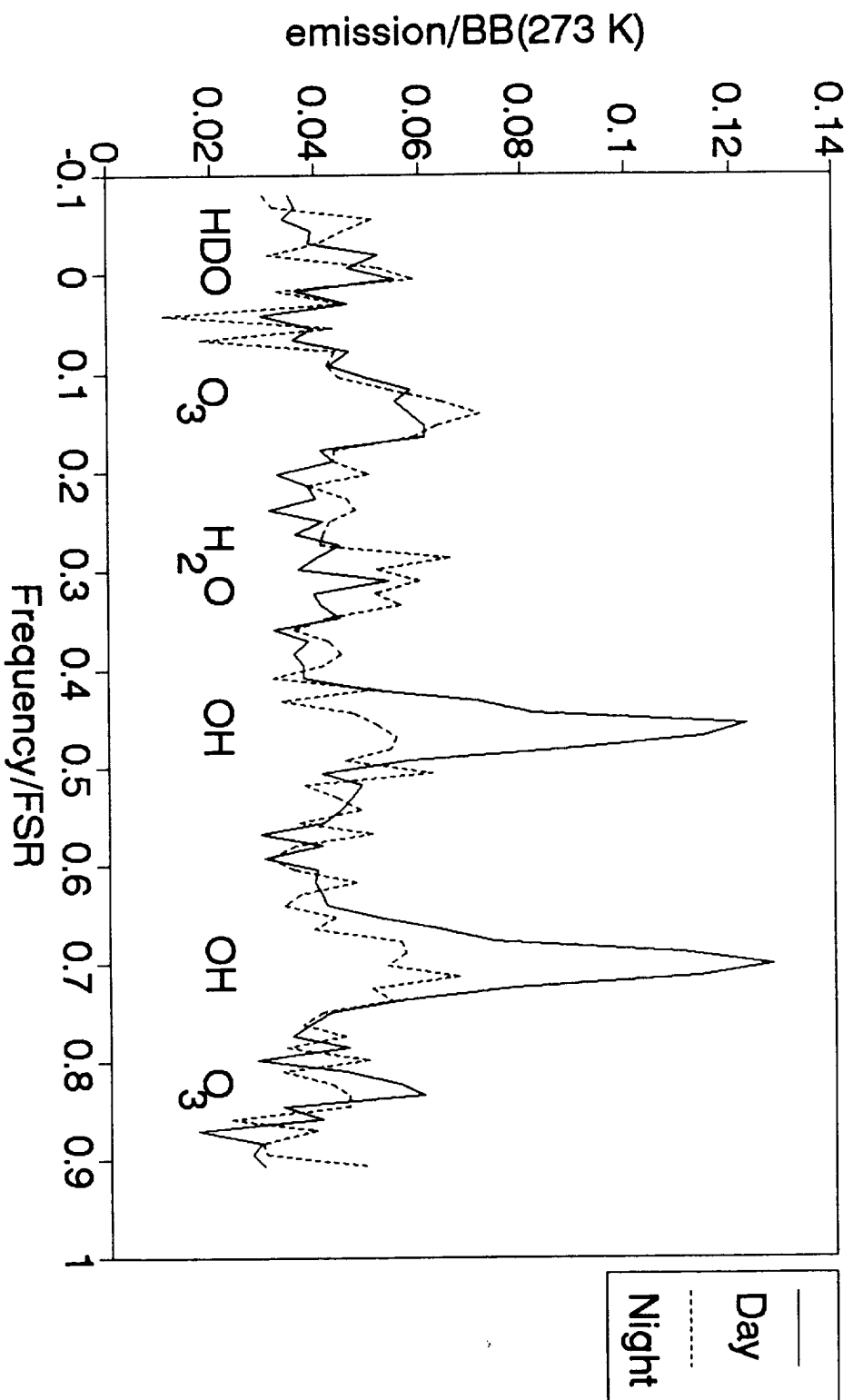
1. D. B. Peterson and H. M. Pickett, "A Cryogenic Far-Infrared Fabry-Perot Etalon", Applied Optics, in press, 1991.

Additional publications on the instrument design and OH results are in preparation and will be submitted to journals in the coming year.



# Atmospheric Spectrum

FILLOS - April 1991



## MULTI-SENSOR BALLOON MEASUREMENTS

Odell F. Raper, Jet Propulsion Laboratory

### OBJECTIVES:

Continuing technical, logistical, and operational support of stratospheric balloon flights is provided to measure the abundance and altitude distribution of a large number of chemical constituents in the upper atmosphere. Two modular gondola systems are available to carry multi-instrument packages, consisting of several JPL remote sensing instruments and instruments from other institutions in the U. S. and abroad. Each payload is normally configured to meet a specific scientific objective. Data are obtained on the altitude profiles for a number of chemically coupled species from simultaneous flights in the same airmass for the purposes of instrument intercomparisons, testing of atmospheric chemical models, and validation of satellite data.

### SUMMARY OF PROGRESS AND RESULTS

A turnaround flight was made in the Spring of 1990 from Ft. Sumner, New Mexico which included FILOS, BMLS, FIRS, and the Margitan ozone experiment. In the Fall of that year two gondolas were launched, one carrying FILOS, Mark IV, and the ozone experiment, and the other carrying the Italian far infrared interferometer (IBEX) flown by Bruno Carli. During 1990 both a new command system and a new azimuth drive system were designed and implemented.

In the Spring of 1991 a flight was mounted from Daggett, California with the new microwave balloon instrument (SLS), FILOS, and the ozone instrument. This flight was a scientific success but extensive damage was inflicted on the gondola as a result of chute drag after landing. Remarkably, damage to the science instruments was minimal. Later in the Spring, a successful turnaround flight was made with the Mark IV from Ft. Sumner. Both a sunset and sunrise transition were recorded by the instrument during this flight.

For the Fall of 1991, the balloon group will support a flight of the JPL complement of instruments consisting of the ozone instrument, FILOS, and SLS during the turnaround from Ft. Sumner.

### C. GROUND-BASED MEASUREMENTS



**TITLE OF RESEARCH TASK:** Collecting, Analyzing and Archiving of Ground Based Infrared Solar Spectra Obtained from Several Locations.

**INVESTIGATORS:** David G. Murcray, Physics Department, University of Denver  
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William P. Chu, NASA Langley Research Center  
Curtis P. Rinsland, NASA Langley Research Center  
Peter Woods, National Physical Laboratory, England  
W.A. Matthews, Dept. of Sci. and Indust. Res., New Zealand  
P.V. Johnston, Dept. of Sci. and Indust. Res., New Zealand

**ABSTRACT OF RESEARCH OBJECTIVES:**

The infrared solar spectrum as observed from the ground under high resolution contains thousands of absorption lines. The majority of these lines are due to compounds that are present in the Earth's atmosphere. Ground based infrared solar spectra therefore contain information concerning the composition of the atmosphere at the time the spectra were obtained. The objective of this program is to record solar spectra from various ground locations, and to analyze and archive these spectra. The analysis consists of determining, for as many of the absorption lines as possible, the molecular species responsible for the absorption, and to verify that current models of infrared transmission match the observed spectra. Archiving is an important part of the program since a number of the features in the spectra have not been identified. At some later time, when the features are identified, it will be possible to determine the amount of that compound that was present in the atmosphere at the time the spectrum was taken.

**SUMMARY OF PROGRESS AND RESULTS:**

Ground based observations of stratospheric constituents have proven to be a valuable technique for the detection of trends in the compounds affecting stratospheric ozone. The Network for the Detection of Stratospheric Change is being established to obtain such data at several stations to obtain data over a range of latitudes. A significant portion of the work on this program has been associated with tasks pertinent to implementing the network. One of the instruments which will go to make up the complement of instruments at each site is a high resolution solar interferometer system. During the period covered by this report we constructed the first system and have been operating it in Denver prior to installing it at Mauna Loa (the first U.S. network site). The instrumentation consists of an interferometer system capable of a theoretical resolution of  $0.002 \text{ cm}^{-1}$  (unapodized). The interferometer is coupled to a solar tracking system in order to obtain the desired high resolution solar spectral

data. The building which will house the instrumentation at the Mauna Loa Observatory will not be completed until next year. A small dome is currently available and a similar system requiring less room was installed in this dome during early May. This instrumentation will be operated on an expedition basis until the building is completed. The first such expedition was undertaken the week of July 8-12. Solar spectra were taken on several days during this period including before and after the total eclipse on July 11.

Part of the work to be accomplished for the network is to develop the software which will be used to analyze the solar spectra obtained with the network instrumentation. The high resolution available in these spectra allows one to retrieve some profile information concerning the constituent. The amount of altitude information depends on the spectral region and constituent. Currently there is no accepted program for retrieving these data. The data sets being obtained will be used to develop these retrieval methods.

#### PUBLICATIONS:

Murcray, F.J., F.H. Murcray, A. Goldman, R.D. Blatherwick and D.G. Murcray, "High-Resolution Studies of Atmospheric IR Emission Spectra," SPIE 1991, April 1-5, Orlando, Florida.

Blatherwick, R.D., F.J. Murcray, D.G. Murcray and M.H. Locker, "Determination of the Altitude of the Nitric Acid Layer from Very High Resolution Ground-Based IR Solar Spectra," SPIE 1991, April 1-5, Orlando, Florida.

Murcray, F.J. and R. Heuberger, "Infrared Atmospheric Absorption and Emission Measurements," Antarc. J., in press, 1990.

McElroy, C.T., A. Goldman, P.F. Fogal and D.G. Murcray, "Heterodyne Spectrophotometry of Ozone in the 9.6- $\mu$ m Band using a Tunable Diode Laser," J. Geophys. Res., 95, 5567-5575, 1990.

**THE MEASUREMENT OF STRATOSPHERIC TRACE GASSES BY  
mm-WAVE EMISSION SPECTROSCOPY**

**Principal Investigator:** Dr. Robert L. de Zafra  
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**Research Objective:** This program covers both the upgrading of an existing ground-based mm-wave emission spectrometer, and the development and deployment of a new mm-wave spectrometer with increased sensitivity, for the quantitative measurement of selected stratospheric trace gases at various field locations. The trace gases of primary interest for this project are ClO, N<sub>2</sub>O, O<sub>3</sub>, HO<sub>2</sub>, and HCN.

**Progress and Results:** The previously existing Stony Brook mm-wave spectrometer has been improved by redesigning the local oscillator injection system for its heterodyne receiver. The new quasi-optical injection system is geometrically simpler than that previously employed, and allows use of larger (3" rather than 2" diameter) mirrors and apertures. This appears to have materially reduced residual baseline ripple of instrumental origin. Use of the instrument for observations has been unfortunately limited since this improvement was completed, due to (a) quite poor atmospheric conditions during planned observing periods at the Mauna Kea Observatory, (b) administrative decisions at the Observatory which have recently halted observations until a new facility is completed, and (c) a heavy involvement of available personnel in the task of constructing an entirely new receiver system based on superconducting tunnel junction technology.

This second objective - creation of an entirely independent mm-wave spectrometer with improved sensitivity - has consumed most of our effort over the past 18 months. The detector employs a Nb-AlO-Nb superconducting tunnel junction with an area of about 1 square micron, fabricated by us at Stony Brook. This is mounted in a mixer block which follows a Cal Tech design. The detector, along with an ultra-low-noise HEMT amplifier, is maintained at 4.5 K by a closed-cycle He refrigerator. The overall receiver package, with associated electronics, is contained in a rather compact package compared to our earlier instrument. (This is compensated in part by the unfortunately much larger size and weight of the closed-cycle refrigeration system required for 4.5 K operation instead of the previous 20 K.) The receiver system employs built-in hot and cold load black-body calibration sources, to make calibration faster and simpler, and minimize the need for auxiliary supplies of liquid nitrogen in field.

Lab tests have to date yielded a best-value receiver noise temperature of about 255 K, with typical results of about 300 K. This is by far the best performance achieved for any mm-wave atmospheric spectrometer to date in this frequency range (>200 GHz), and compares well with the most sensitive receivers yet deployed for radio astronomy in this range. It marks somewhat better than a factor of 2 (typical) improvement over our previous best receiver noise temperature. This improvement will reduce integration times by about a factor of 4. The extremely weak emission intensity from stratospheric ClO, for instance, has previously required tens of hours to reach acceptable S/N ratios. For this diurnally varying species, this has meant total integration periods that can stretch over several days even under very good

observing conditions. The new system should allow single-day observations of ClO with a time resolution of 2 hours, under very good observing conditions (i.e. very low atmospheric opacity, requiring very low tropospheric water vapor). We believe that further junction improvements may give us reliable receiver noise temperatures of 200 K or less within the next year.

At this writing (Aug. 1991) the system is in transit to McMurdo Station, Antarctica where we will set it up for observations of the Antarctic ozone hole starting about the first of September. Our intent is to measure profiles of ClO, N<sub>2</sub>O and O<sub>3</sub> over the range 17-45 km throughout the period of ozone hole growth, and as far into the recovery period as weather conditions allow.

The earlier system will be used late in the fall of 1991 and into 1992 in a comparison measurements program with a new commercially-made ClO measuring spectrometer intended for the NDSC. The new spectrometer will be used in Greenland and again in Antarctica in 1992-93 as part of the UARS ground-based Correlative Measurements Program.

#### Publications:

- "Measurement of Anomalous ClO Concentration in the Spring Stratosphere over McMurdo Station, 1986 and 1987, and Consequences for Ozone Depletion" R. L. de Zafra, M. J. Jaramillo, J. Barrett, L. Emmons, P. Solomon, and A. Parrish, pp. 49-52, in *Ozone in the Atmosphere: Proceedings of the Quadrennial Ozone Symposium, 1988*; (Deepak Pub. Co. 1990)
- "Stratospheric Hydrogen Cyanide Measurements at McMurdo Station During the Antarctic Spring", M. Jaramillo, R. L. de Zafra, J. Barrett, L. K. Emmons, P. M. Solomon, and A. Parrish, pp. 58-60, in *Ozone in the Atmosphere: Proceedings of the Quadrennial Ozone Symposium, 1988*; (Deepak Pub. Co. 1990)
- "Measurement of Atmospheric Opacity at 278 GHz at McMurdo Station, Antarctica in Austral Spring Seasons, 1986 and 1987", R. L. de Zafra, M. Jaramillo, J. Barrett, L. K. Emmons, A. Parrish, and P. M. Solomon, *Int. J. Infrared and Millimeter Waves*, **11**, 463-367, 1990.
- "Observation of a Strong Inverse Temperature Dependence for the Opacity of Atmospheric Water Vapor in the mm Continuum near 280 GHz." L. K. Emmons and R. L. de Zafra, *Int. J. Infrared and Millimeter Waves*, **11**, 469-488, 1990.
- "Measurement of the Cooling Capacity of an RMC-Cryosystems Model LTS 4.5-025 Closed-Cycle Helium Refrigerator", R. L. de Zafra, W. H. Mallison, L. K. Emmons, and D. Koller, *Rev. Sci. Instruments*, **62**, 1309-1310, 1991.
- "Procedure for Computer-Controlled Milling of Accurate Surfaces of Revolution for Millimeter and Far-Infrared Mirrors", L.K. Emmons and R. L. de Zafra, *Applied Optics*, (in press).



**A. Global Atmospheric Gases Experiment (GAGE): Coordination, Data Processing, Scientific Analysis, and Barbados Station**

**B. Principal Investigator**

Ronald G. Prinn, MIT Rm. 54-1312, Cambridge, MA 02139. See also the companion report for GAGE: Samoa and West Coast stations, Calibration, and New Instrumentation, Ray F. Weiss, Scripps Institution of Oceanography, Principal Investigator.

**Co-Investigators**

Fred N. Alyea and Derek M. Cunnold, Georgia Institute of Technology, Atlanta, GA 30332; Peter G. Simmonds, INSCON, United Kingdom.

**C. Research Objectives**

Continuous high frequency gas chromatographic measurements of two biogenic/anthropogenic gases ( $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ) and 5 anthropogenic gases ( $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CF}_2\text{ClCFCl}_2$ ,  $\text{CCl}_4$ ) are carried out at globally distributed sites in order to determine quantitatively the source and sink strengths and circulation of these chemically and radiatively important long-lived gases.

**D. Summary of Progress and Results**

The data for the 7 long-lived gases measured in GAGE during 1990-1991 continue generally to be of good quality. One of the GAGE stations (Cape Meares, OR) has now been phased out and is planned to be replaced by a new station at Trinidad Head, CA. Ten years of ALE-GAGE data for nitrous oxide ( $\text{N}_2\text{O}$ ) have been analyzed and published. The data indicate significant tropical sources for  $\text{N}_2\text{O}$ ; specifically 32-39% of global emissions occur from  $30^\circ\text{N} - 0^\circ$  and 20 - 29% from  $0^\circ - 30^\circ\text{S}$  with sources in the  $30^\circ\text{N} - 90^\circ\text{N}$  region like fossil fuel combustion therefore playing a much smaller role than previously thought. Twelve years of ALE-GAGE data for methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ) have been analyzed and submitted for publication. The data indicate a global-average lifetime for  $\text{CH}_3\text{CCl}_3$  of 5.7 (+0.7, -0.6) years, a weighted-average hydroxyl radical ( $\text{OH}$ ) concentration of  $(8.7 \pm 1.0) \times 10^5$  radical  $\text{cm}^{-3}$ , and a trend in this  $\text{OH}$  of  $1.0 \pm 0.8\%$  per year. The  $\text{CH}_3\text{CCl}_3$  measurements at Samoa show a remarkable correlation with the El Nino-Southern Oscillation (ENSO) which we attribute to ENSO-related circulation changes. A critical comparison of ALE-GAGE  $\text{CH}_3\text{CCl}_3$  tropical data with a three-dimensional global circulation model and a clarifying comment on ALE-GAGE inversion methods are both in press.

**E. Journal Publications**

R. Prinn, D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser, and R. Rosen, 1990. Atmospheric emissions and trends of nitrous oxide deduced from 10 years of ALE-GAGE data. *J. Geophys. Res.*, **95**, 18369-18385.

D. Hartley and R. Prinn, 1991. Comment on "Tropospheric OH in a three-dimensional chemical tracer model: An assessment based on observations of  $\text{CH}_3\text{CCl}_3$ " by C.M. Spivakovsky et al. *J. Geophys. Res.*, in press.

D. Cunnold and R. Prinn, 1991. Further comment on "Tropospheric OH in a three-dimensional chemical tracer model: An assessment based on observations of  $\text{CH}_3\text{CCl}_3$ " by C.M. Spivakovsky et al. *J. Geophys. Res.*, in press.

R. Prinn, D. Cunnold, P. Simmonds, F. Alyea, R. Boldi, A. Crawford, P. Fraser, D. Gutzler, D. Hartley, R. Rosen, and R. Rasmussen, 1991. Global average concentration and trend for hydroxyl radicals deduced from ALE/GAGE trichloroethane (methyl chloroform) data for 1978-1990. *J. Geophys. Res.*, in press.

A. Title of Research Task

Global Atmospheric Gases Experiment (GAGE): Calibration, New Instrumentation and Station Operations

B. Investigator and Institution

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C. Abstract of Research Objectives

This project is a component of the multi-national global atmospheric trace species measurement program entitled "Global Atmospheric Gases Experiment" (GAGE), and covers instrumentation development and calibration for the international program and station operations for the U.S. program. A separate grant to R. G. Prinn at the Massachusetts Institute of Technology covers interpretive work in the U.S. GAGE program. The case for real-time high-frequency measurement networks of radiatively important and chemically active atmospheric trace species is widely recognized. The program carried out by the Scripps Institution of Oceanography comprises: 1) Continuation and improvement of ongoing gas chromatographic measurements of two biogenic/anthropogenic gases ( $\text{CH}_4$  and  $\text{N}_2\text{O}$ ) and five anthropogenic gases ( $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CF}_2\text{ClCFCl}_2$  and  $\text{CCl}_4$ ) at four globally distributed stations and at one new station to be opened in the near future; 2) The development and dissemination of accurate primary and secondary calibration standards for each of the above gases, including periodic renewal of these standards to minimize effects of standard instability and instrument non-linearity; and 3) Operation of the U.S. GAGE station at Samoa and the establishment of a new U.S. station once new instrumentation development and fabrication are completed.

D. Summary of Progress and Results

Progress in the research carried out at Scripps during 1990 and 1991 under NAGW-2034 "Global Atmospheric Gases Experiment (GAGE)" has been significant. The principal accomplishments have been: 1) The conceptual and engineering design of the new-generation GAGE instruments, including a novel pressure-programming approach to allow on-site non-linearity correction measurements for each GAGE gas and thus permit use of working standards with concentrations differing significantly from ambient values without degrading the accuracy of the measurements; 2) The preliminary testing and confirmation of the pressure-programming approach using existing instruments; 3) Beginning the fabrication of the first new instrument, including the purchase of the major instrumental components, construction of the custom sampling module which is the heart of the new

system, and implementation of new computer software for instrument control, data acquisition, and peak integration; 4) The initial experimentation with GAGE primary standard preparations for  $\text{CF}_2\text{ClCFCl}_2$  and preliminary design of a new GAGE primary standard preparation system using oil-free vacuum pumps, a vacuum/pressure system constructed of electropolished stainless steel, a quartz spiral manometer, existing dilution volumes, and an existing mercury manometer; 5) The successful startup and operation of the Samoa Hewlett-Packard 5880 instrument to collect data at that station until the new GAGE instruments are ready for field operations; and 6) The preparation of dry air secondary standards ("cal-gases") for all the GAGE stations, compressed at La Jolla and in the interim calibrated by P. Fraser against previous GAGE standards from OGC which are archived at Cape Grim.

The new GAGE instrument consists of a Hewlett-Packard 5890 chromatograph with two electron capture detectors, a Carle chromatograph with a single flame ionization detector, and most-importantly a custom-designed and fabricated thermostatted sample module containing the gas sample valves, backflushing valves, stream selection valve, Nafion drier, and pressure programming equipment. These components are now being fabricated into a single instrument, with four separate heated zones. Data acquisition will be on a single small Sun workstation computer, where all the chromatograms will be stored digitally and integrated, and where all the instrument operations including sample injections and non-linearity calibrations will be controlled.

In December 1990, after considerable negotiation with NOAA, NASA and the Oregon Graduate Center (OGC), we restarted operations at the U.S. GAGE station in Samoa. This station had been closed by OGC in early 1990. Restarting the HP 5880 chromatographic system at this station proved to be a formidable task. There were numerous hardware failures in the system, which had previously been allowed to operate without protection from the atrocious island electrical power. We provided a new uninterruptible AC power supply for the entire system, repaired the chromatograph and its associated computer, and restarted the system without the benefit of computer source code or current object code. The station is now in reasonable operation, despite some down time due to the failure of the diesel generator at the NOAA station in April 1991 and some contamination problems resulting from the long period in 1990 when the station was not operated.

#### E. Journal Publications

The Scripps involvement in the GAGE project has only recently begun. There are not yet any publications resulting from this involvement.

- A. Latitudinal Gradients in Tropospheric Concentrations of Selected Halocarbons and Hydrocarbons (NAGW-452)
- B. Professor F. Sherwood Rowland, Department of Chemistry, University of California, Irvine, California 92717
- C. The primary goal of this project is the understanding of the global sources, sinks, and distribution of volatile gaseous trace species. The basic experimental input for these studies is the measurement of the atmospheric mixing ratios of numerous halocarbons (CFCs, especially  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{CCl}_2\text{FCClF}_2$ ;  $\text{CH}_3\text{CCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CCl}_2=\text{CCl}_2$ ,  $\text{CHCl}=\text{CCl}_2$ , and others, hydrocarbons ( $\text{CH}_4$ , alkanes to  $\text{C}_{14}\text{H}_{30}$ ,  $\text{C}_2\text{H}_2$ , several olefins), and carbon monoxide every several months on a regular grid from  $71^\circ\text{N}$  (Barrow, Alaska) to  $47^\circ\text{S}$  (New Zealand). Improvements during 1991 in the sensitivity of our analytical techniques have greatly extended the number of halocarbon compounds for which we now have high precision data. These additional compounds include  $\text{CClF}_2\text{CClF}_2$  and  $\text{CClF}_2\text{CF}_3$  (CFCs 114 & 115),  $\text{CHClF}_2$  (HCFC-22),  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CH}_3\text{I}$ . The air samples are collected at ground level in remote locations, away from sources of these compounds, and then returned to the home laboratory for analysis by gas chromatography. The measurements provide information about the growth in atmospheric mixing ratios for the longer lived species (e.g.  $\text{CH}_4$ , all of the CFCs,  $\text{CCl}_4$ ,  $\text{CH}_3\text{CCl}_3$ ). They also demonstrate the pronounced seasonal and latitudinal mixing ratio differences found for molecules such as  $\text{CO}$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$  which have atmospheric lifetimes of less than one year. Sampling at numerous remote oceanic sites provides information about oceanic biological sources of compounds such as the methyl halides,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$ . Correlation among the mixing ratios of different compounds provides details about source and sink relationships. Global average mixing ratios are calculated for the longer-lived molecules from the average concentrations in 16 equal area latitudinal bands.
- D. Our measurements of the globally-averaged mixing ratios of methane have shown a monotonic increase from 1.52 ppmv in January 1978 to 1.74 ppmv in December 1991, for a yearly average increase of 0.016 ppmv over 13.9 years. The best fit to this data series indicates a general slowing of the yearly rate of increase from about 0.018 ppmv in the early 1980s to 0.010-0.012 in the 1990s. No substantial deviations have been found for isolated geophysical events such as volcanic eruptions of El Chichon and Pinatubo, or for El Nino conditions. The one-sigma standard error for a smoothed curve fit to the data is 0.003 ppmv for 40 data periods.

Our data for  $\text{CCl}_2\text{FCClF}_2$  (CFC-113) continue to display a rapidly increasing atmospheric mixing ratio, having risen from a global average of about 13 pptv in 1977 to about 80 pptv in late 1991. The data have now been calibrated on an absolute basis. Our improved sensitivity now allows the detection of about 80 halocarbon molecules with no more than 2 or 3 carbon atoms even in moderately remote U.S. locations (Rocky Mountains).

The global increase in the concentrations of  $\text{CCl}_2\text{F}_2$  (CFC-12) and  $\text{CCl}_3\text{F}$  (CFC-11) has continued, but a marked slowing<sup>2</sup> in the rate of increase is detectable in the 1991 data for each, as anticipated from the provisions of the United Nations Montreal Protocol.

The strong seasonal variation in  $\text{C}_2\text{H}_6$  mixing ratios continues, consistent with a source almost entirely<sup>2</sup> in the northern hemisphere land masses, and reaction with hydroxyl radical as the only major sink. The seasonal variation for  $\text{C}_2\text{H}_6$  is about a factor of 2.5 in each hemisphere, with maximum mixing<sup>2</sup> ratios in the winter. The northern winter concentrations are in the range 2.0-3.0 ppbv, while the southern summer values generally fall to 0.2 ppbv or less. On the basis of more than 5 years of CO measurements, the surface level northern hemispheric mixing ratios peak at about 150 ppbv in temperate latitudes, decreasing to 80 ppbv in the summer. The southern hemispheric mixing ratios are smaller, ranging between about 40 and 60 ppbv. The southern hemispheric values are consistent with the oxidation of methane as its major precursor, while the higher northern concentrations include direct emission of CO and oxidation of other hydrocarbons.

The choice of "remote" sampling sites, e.g. Pacific islands, was originally guided by the intention of measuring the background concentrations of anthropogenic chlorocarbon molecules such as the CFCs,  $\text{CCl}_4$  and  $\text{CH}_3\text{CCl}_3$ . These sites are now providing information as well about natural sources of halocarbons, including  $\text{CH}_3\text{I}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$ , all presumably the products of oceanic biological processes.

Latitudinal measurements of the anthropogenic  $\text{CCl}_2=\text{CCl}_2$  have shown a globally-averaged concentration of 5 to 7 pptv. The industrial production of this compound has exceeded that of CFC-12 for the past 3 decades, yet its concentration is only about 1% as large as for the latter, because a powerful tropospheric sink (reaction with HO) exists for this molecule, limiting its atmospheric lifetime to six months.

E. Rowland, F. S. Stratospheric ozone depletion by Chlorofluorocarbons, *Ambio*, 19, 281-292, 1990

Rowland, F. S. Stratospheric ozone depletion, *Annual Review Phys. Chem.*, 42, 731-768, 1991

Rowland, F. S. Chlorofluorocarbons (CFCs) in the Atmosphere: Stratospheric Ozone Depletion and the Greenhouse Effect, Second Symposium on Global Change, American Meteorological Society, p. 87-92.

A. Ground-based Observations and Theoretical Studies of the Vertical Column Abundance of Atmospheric Hydroxyl

B. Co-investigators

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C. Abstract of Research Objectives

The experimental objective of this research is to secure spectroscopic observations of the vertical column abundance of atmospheric hydroxyl (OH). These observations consist of: 1) a continuation of the series of measurements begun in 1977 at Fritz Peak Observatory, Colorado (40°N, 105°W), and 2) a new series of similar measurements at the Department of Scientific and Industrial Research Atmospheric Station at Lauder, New Zealand (45°S, 170°E). The theoretical objective of the project is the analysis and interpretation of the OH data base in order to achieve a more accurate understanding of the photochemistry of the middle atmosphere.

D. Summary of Progress and Results

The daytime spectroscopic observations of the vertical column abundance of hydroxyl at Fritz Peak Observatory continue as atmospheric conditions permit with 2010 data sets secured from August 1989 to August 1991. These measurements have 10-15% uncertainty with time resolution of about 20 minutes. The OH diurnal behavior and its seasonal variation, as well as the annual and semiannual periodicities, continue as observed in previous years. Average abundances increased about 8% during the approach to the maximum of solar cycle 22 and have subsequently decreased about 2%. Observations at Lauder, New Zealand, were initiated in May 1990 by Dr. S.W. Wood, Postdoctoral Research Associate. As of August 1991, 300 data sets had been obtained. Average OH levels are about 11% higher than in Colorado and exhibit a similar diurnal variation. A more detailed characterization of its behavior would be premature in view of the relatively small number of observations.

Analysis of all post-1979 Colorado morning data at zenith angles  $>45^\circ$  shows monthly departures from the 1980-1988 average distribution which have a dominant covariance with the monthly average total ozone measured at Boulder, Colorado. See Figure 1. The magnitude of this seasonal OH variation, relative to the observed enhancement in OH abundance since 1980, is about 40%. This is approximately equal to the magnitude of the seasonal variation of total ozone in the 15-25 km region. This quantitative agreement is consistent with an hypothesis of a direct dependence of the post-1980 enhancement in OH on the ozone abundance in the lower stratosphere. Departures from the  $\Delta\text{OH}-\int\text{O}_3$  column: an annual variation of 3% amplitude and a semiannual variation of 7% amplitude. These variations are in phase at the winter solstice. See Figure 2. The PM-AM OH abundance differences for zenith angles  $>45^\circ$  characterize the OH diurnal behavior. These differences covary with the seasonal change in the reciprocal of Boulder total ozone. See Figure 3. This suggests that the persistent seasonally varying OH diurnal behavior may also occur in the lower stratosphere. The above discussion represents an alternative analysis and new interpretation of the seasonal and diurnal OH behaviors consistently observed during the 1980-91 period.

Our steady-state calculations for [OH] at each level in the stratosphere and mesosphere using currently accepted photochemistry yields a column OH zenith-angle dependence which agrees with that obtained by other modelers; it

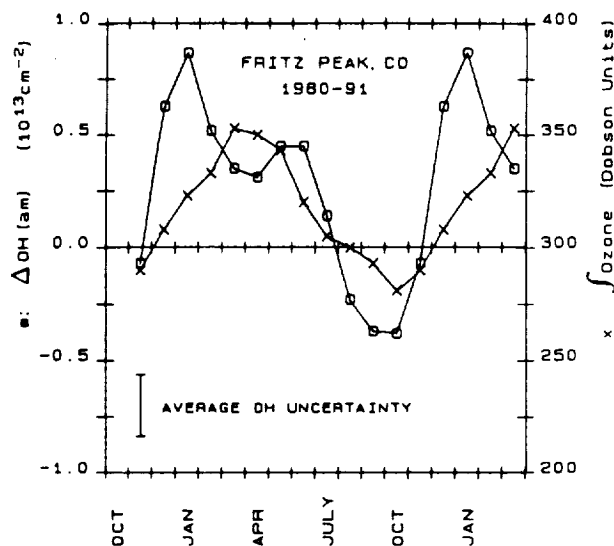


Figure 1

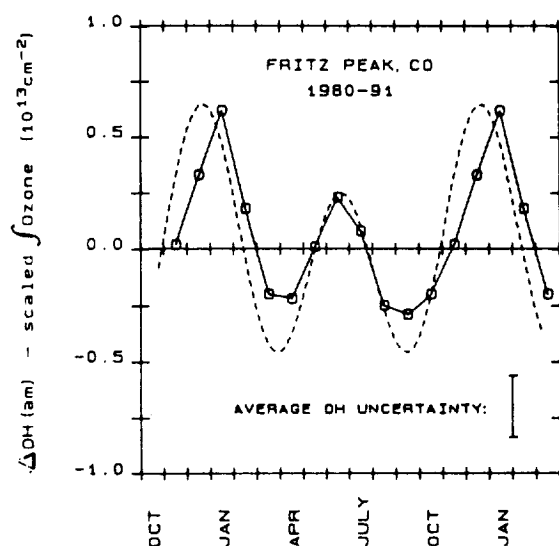


Figure 2

also agrees with our 1977-79 observations. Additional study reveals that the steeper dependence of the OH data observed since 1980 can be reproduced very well by postulating lower stratospheric conditions which would permit OH concentrations to vary linearly with the ozone photolysis producing  $O(^1D)$  for reaction with  $H_2O$ . The addition of an OH contribution from the lower stratosphere to that predicted by currently accepted photochemistry for the upper stratosphere and mesosphere yields encouraging agreement with the OH zenith-angle dependence observed since 1980. See Figure 4.

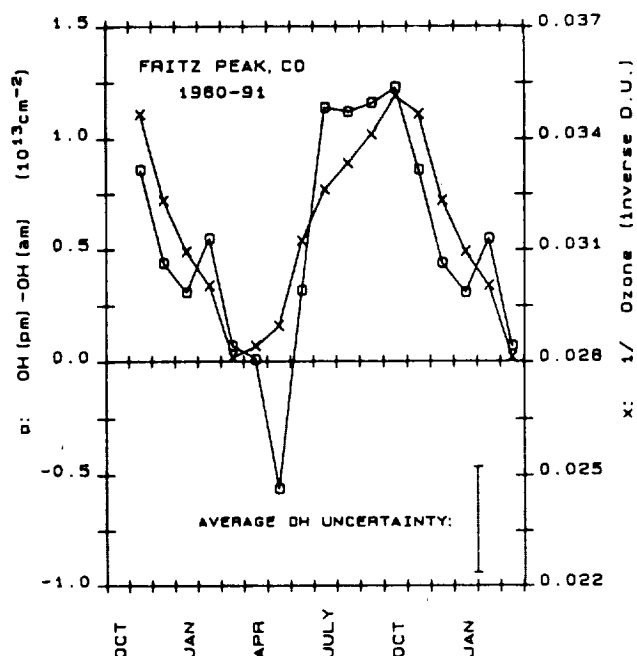


Figure 3

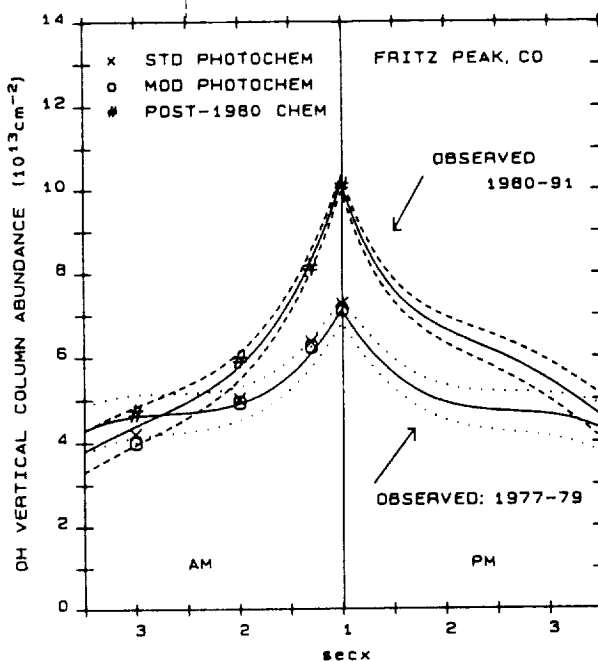


Figure 4

#### E. Journal Publications

Burnett, C.R., K.R. Minschwaner, and E.B. Burnett, "OH Vertical Column Abundance: Tropical Measurements", J. Geophys. Res., 95, 16491-16495, 1990.



## **A. NDSC DIFFERENTIAL ABSORPTION LIDAR**

### **B. Principal Investigator : Dr. I. Stuart McDermid**

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California 92397-0367

### **C. Research Objectives**

The object of this project has been the establishment of a facility at the JPL-Table Mountain Facility (TMF), Wrightwood, California, from which to make long-term atmospheric measurements. The laser remote sensing technique of differential absorption lidar (DIAL) is being used to derive atmospheric ozone concentration profiles. Regular measurements began in 1988 and are continuing in order to provide a long-term record to aid in the detection of trends and changes in the ozone concentration and its vertical distribution. A new system is currently under development for installation in the Network for Detection of Stratospheric Change (NDSC) at the Mauna Loa Observatory (MLO), Hawaii. It is expected that the lidars at TMF and MLO will play an important role in the correlative measurements program related to the Upper Atmosphere Research Satellite (UARS).

### **D. Progress and Results**

The JPL-TMF facility has played an important role in the development and testing of new instruments for the Network for Detection of Stratospheric Change (NDSC). Stratospheric ozone profiles have been obtained on a routine basis since January 1988 and over 300 independent measurements has been made by the end of 1990. The lidar has been evaluated by inter-comparison with a number of ozone measuring systems and techniques which has confirmed its ability to make precise and accurate measurements of the ozone concentration profile from 15 km to >45 km altitude. The new system being developed for MLO is expected to make the first measurements in January 1992.

### **E. Publications**

**I. S. McDermid, S. M. Godin, Pi-Huan Wang and M. P. McCormick.**

J. Geophysical Research, 1990, 95, 5605-5612.

Comparison of Stratospheric Ozone Profiles and Their Seasonal Variations as Measured by LIDAR and SAGE II During 1988.

**I. S. McDermid, S. M. Godin, R. A. Barnes, C. L. Parsons, A. Torres, M. P. McCormick, W. P. Chu, P. Wang, J. Butler, P. Newman, J. Burris, R. Ferrare, D. Whiteman and T. J. McGee.**

J. Geophysical Research, 1990, 95, 10037-10042.

Comparison of Ozone Profiles From Ground-Based Lidar, ECC Balloon Sonde, ROCOZ-A Rocket Sonde, and SAGE II Satellite Measurements.

- I. S. McDermid**, S. M. Godin and L. O. Lindqvist.  
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Ground-Based Laser DIAL System for Long-Term Measurements of Stratospheric Ozone.
- D. A. Haner and I. S. McDermid.**  
IEEE J. Quantum Electronics, 1990, QE-26, 1292-1298.  
Stimulated Raman Shifting of Nd:YAG Fourth Harmonic (266 nm) in H<sub>2</sub>, HD and D<sub>2</sub>.
- I. S. McDermid**, S. M. Godin, L. O. Lindqvist, T. D. Walsh, J. Burris, J. Butler, R. Ferrare, D. Whiteman and T. J. McGee.  
Applied Optics, 1990, 29, 4671-4676.  
Measurement Inter-Comparison of the JPL and GSFC Stratospheric Ozone Lidar Systems.
- D. Rees and I. S. McDermid.**  
Applied Optics, 1990, 29, 4133-4144.  
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- T. J. McGee**, P. Newman, R. Ferrare, D. Whiteman, J. Butler, J. Burris, S. M. Godin and **I. S. McDermid.**  
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Lidar Observations of Ozone Changes Induced by Sub-Polar Airmass Motion Over Table Mountain (34.4° N).
- I. S. McDermid**, S. M. Godin and T. D. Walsh.  
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- I. S. McDermid** and W. B. Williamson.  
NASA Tech Briefs, 1990, 14(12), 28.  
Beam-Stop for High Power Lasers.
- J. J. Tsou**, B. J. Connor, A. D. Parrish, **I. S. McDermid**, and W. P. Chu.  
Eos, Transactions, American Geophysical Union, 1990, 71(43), 1247.  
Intercomparison of Middle Atmospheric Ozone Profiles Measured by Millimeter Wave Radiometer, Lidar, and SAGE II Satellite.
- I. S. McDermid**, D. A. Haner, M. M. Kleiman, T. D. Walsh and M. L. White.  
Optical Engineering, 1991, 30, 22-30.  
Invited Paper for the Special Issue on Lidar.  
Differential Absorption Lidar Systems at JPL-TMF for Tropospheric and Stratospheric Ozone Measurements.
- I. S. McDermid** and T. D. Walsh.  
Jet Propulsion Laboratory Document, JPL D-8354, March 1991.  
Surface Ozone Concentrations at Table Mountain Facility (34.4° N, 117.7° W) During 1989 and 1990.

## GROUND-BASED LIDAR MEASUREMENTS OF STRATOSPHERIC OZONE AND TEMPERATURE

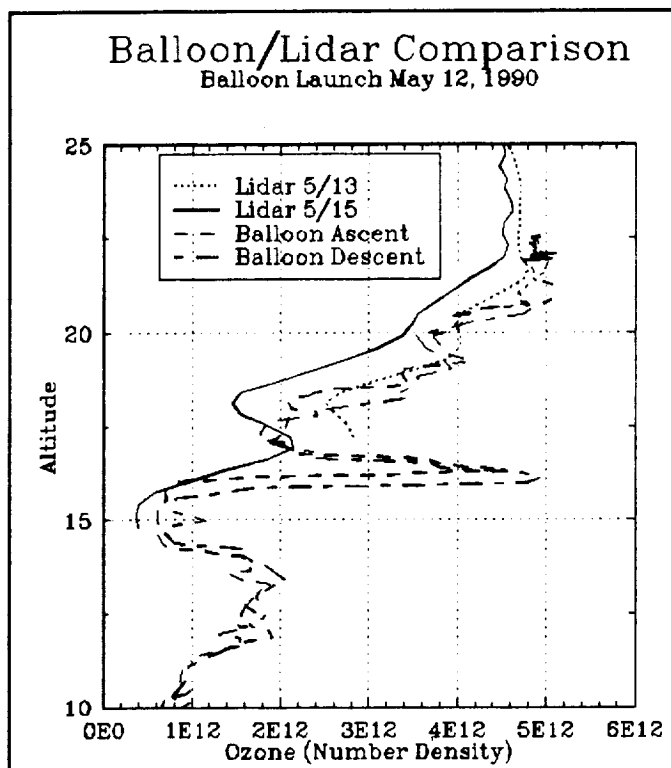
Thomas J. McGee  
Paul Newman  
Laboratory for Atmospheres  
Goddard Space Flight Center  
Greenbelt, MD 20771

**Research Objectives.** The primary objective is the measurement of high precision vertical profiles of ozone and temperature. The instrument is a ground-based Differential Absorption Lidar (DIAL) housed in a 45' trailer. Ozone measurements are made between 20 and 50 km, and temperature is measured between 30 and 65-70 km. A second instrument is being developed for measurements of temperature and aerosols. This instrument, which is also designed to be mobile, will be capable of measuring a temperature profile from 10 to 80+ km and an aerosol backscattering ratio profile between 10 and 35 km. The ozone lidar has been selected as a Correlative Measurements Instrument for the UARS satellite program. Both instruments are to be active in the newly formed Network for the Detection of Stratospheric Change (NDSC).

### Summary of Progress and Results.

After two successful intercomparisons at Table Mountain, California, the ozone lidar was deployed at Cannon AFB in Clovis, NM to support a balloon flight from nearby Ft. Sumner NM. The balloon carried several instruments which measured ozone, including an in-situ UV spectrometer. The balloon payload was flown on May 12, 1990, but only reached an altitude of 22 km before the balloon itself failed. Lidar data was not available for the night before the balloon launch because of clouds, but data was obtained on the following evening. Figure 1 shows the ascent and descent balloon data along with the two closest nights of lidar data. A thin layer of high concentration ozone was detected at about 16 km in the balloon data. The lidar data from the 13th did not extend that low in the atmosphere, although there is a hint of the layer at the bottom of the profile. The layer is still apparent on the night of the 14th, when lidar data was collected down to 15 km. It can be seen that the agreement between the lidar and the UV spectrometer data is excellent.

After the return of the lidar to Goddard, an extensive modification of the system began. The transmitter was made



**Figure 1.** Comparison of balloon and lidar data following balloon launch from Ft. Sumner, May 12, 1991.

more powerful, the telescope was ground, polished and recoated, the data system was configured to improve the temporal (and therefore vertical) resolution, and most importantly, a mechanical shutter was added to the detector. This has overcome the major weakness in the lidar data, which had been the uncertainty of high altitude measurements due to errors in the determination of the background. When a photomultiplier tube is exposed to a large light signal, a long-lived change in the gain of the tube is induced. This results in an artificially varying background which has in the past been treated by attempting to model the background. The subjective nature of this approach has meant that measurements by this particular lidar were significantly less accurate above 39 km. A series of engineering tests performed at Table Mountain, CA, indicate that the shutter has performed up to expectations, and that now the background can be determined accurately using objective methods which do not require extrapolation back into the data. Measurements are now expected to be made up to 50 km without the systematic error introduced by the previous background treatment.

#### **Publications.**

**"Lidar Observations of Ozone Changes Induced by Sub-Polar Airmass Motion over Table Mountain, CA (34.4N),** T.J. McGee, P. Newman, R. Ferrare, D. Whiteman, J. Butler, J. Burris, S. Godin and I.S. McDermid, *J. Geophys. Res.*, **95**, 20,527, 1990.

**"Measurement Intercomparison of the JPL and GSFC Stratospheric Lidar Systems",** I.S. McDermid, S.M. Godin, L.O. Lindquist, T.D. Walsh, J. Burris, J. Butler, R. Ferrare, D. Whiteman and T.J. McGee, *Applied Optics*, **29**, 4671, 1990.

**"Comparison of Ozone Profiles from Ground-based Lidar, ECC Balloon Sonde, ROCOZ-A Rocket Sonde, and SAGE-II Satellite Measurements",** I.S. McDermid, S.M. Godin, R.A. Barnes, C.L. Parsons, A. Torres, M.P. McCormick, W.P. Chu, P. Wang, J. Butler, J. Burris, P. Newman, R. Ferrare, D. Whiteman and T.J. McGee, *J. Geophys. Res.*, **95**, 10,037, 1990

**"STROZ LITE: NASA Goddard Stratospheric Ozone Lidar Trailer Experiment",** T.J. McGee, D. Whiteman, R. Ferrare, J. Butler and J.F. Burris, *Optical Engineering*, **30**, 31, 1991.

**"Quenching and Rotational Transfer Rates in the  $v'=0$  Manifold of OH",** J. Burris, J. Butler, T.J. McGee and W.S. Heaps, *Chemical Physics*, **151**, 233, 1991.

# Millimeter Wave Ozone Measurements for the Network for Detection of Stratospheric Change

## Co-Principal Investigators:

Dr. Brian J. Connor, NASA Langley Research Center  
Dr. Alan Parrish, University of Massachusetts

## Research Objectives

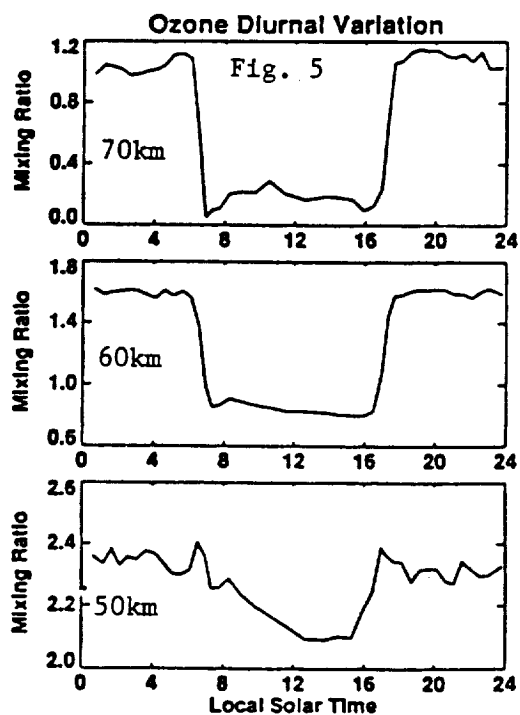
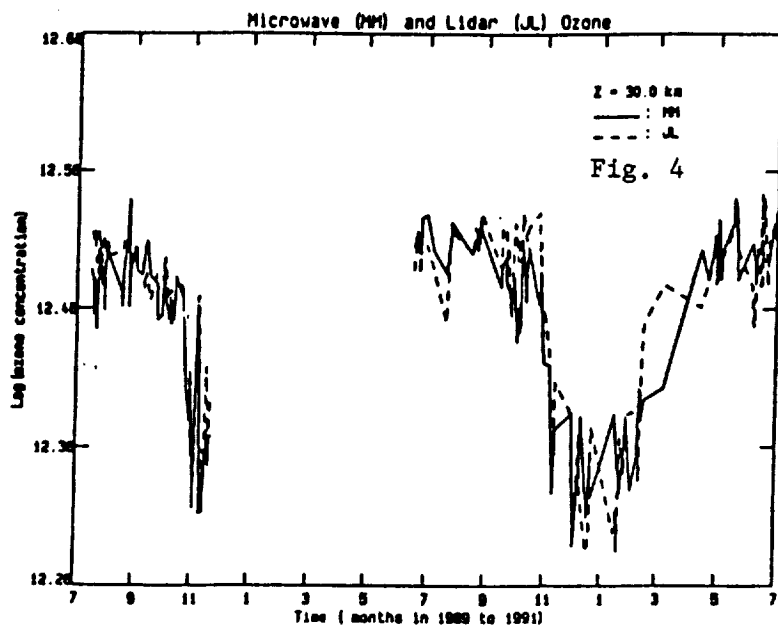
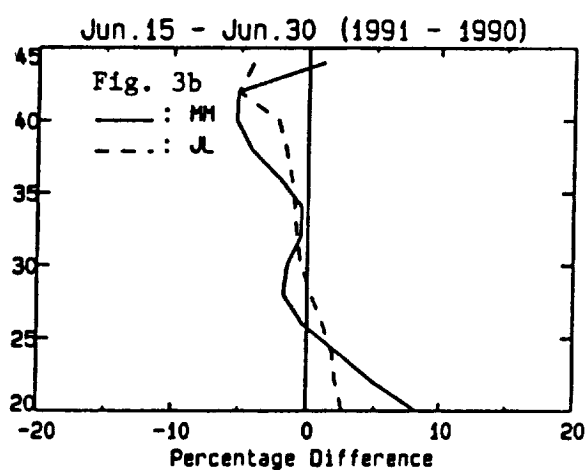
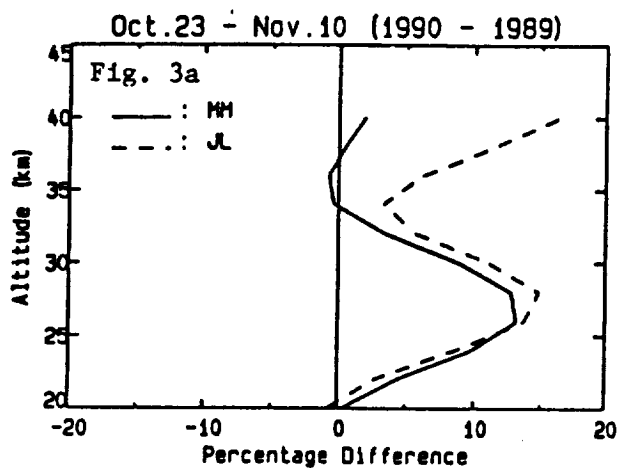
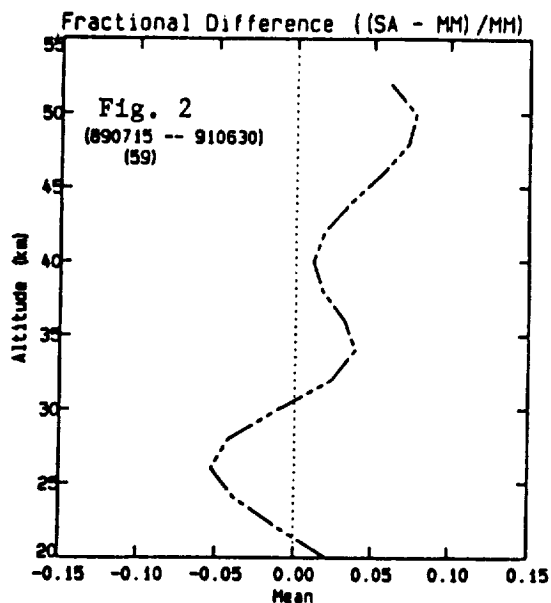
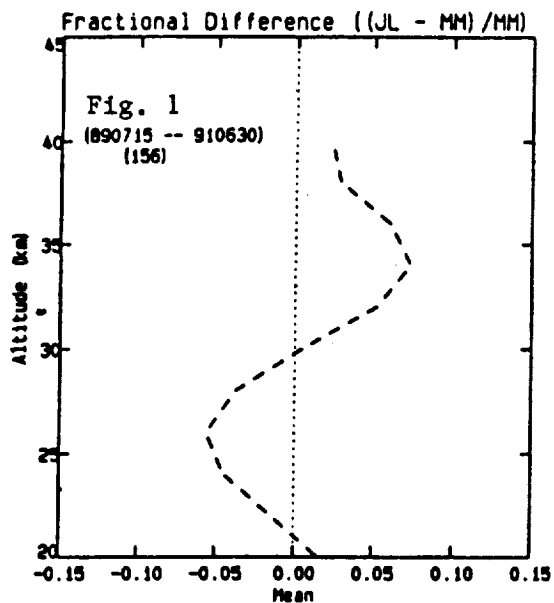
The primary, long-term, objective is to perform monitoring of stratospheric ozone by means of ground-based millimeter wave spectroscopy in order to, first, detect any secular trend in stratospheric ozone abundance independently of other measurements made for this purpose, and second, to provide correlative measurements for existing and future satellite measurements of ozone. The more immediate goal has been to test and refine the capabilities and performance of the existing instrument and data analysis procedures, primarily using intercomparisons with other co-located measurements over a time span of approximately two years. A second objective is to perform scientific studies using the mm-wave data, including studies of the diurnal and seasonal variations of ozone, and the possible coupling of these variations with changes in other geophysical parameters, such as temperature and water vapor.

## Progress to Date

The instrument, which was developed at the Millitech Corporation, was installed at the Table Mountain Observatory in California and operated from July to November, 1989 and has been operating from May, 1990 to the present. It was out of service from November, 1989 to May of 1990 for modifications. Except for this interval, the instrument has been operating nearly continuously on a semiautomatic basis. It produces a spectrum every 20 minutes, and an ozone profile is retrieved either from each spectrum, for measurements of diurnal variations, or from an average of about twenty spectra, for intercomparisons. We have intercompared the mm-wave data with data from the co-located JPL lidar (see report by I. S. McDermid and his colleagues in this volume), and with all data from SAGE satellite overpasses within 1000 km of Table Mountain. Sample results are shown in the figures. Figure 1a shows that the average fractional difference between the mm-wave and lidar measurements is less than 7% between 20 and 40 km. Figure 2 compares the mm-wave and SAGE measurements; where the average fractional difference is less than 8% between 20 and 52 km. Figure 3 demonstrates that the interannual fractional differences between ozone profiles measured by the mm-wave and lidar instruments are typically similar, within a few percent over most of the 20 to 40 km altitude range. Figure 4 displays a time series of mm-wave and lidar data for 30 km altitude over two years, and show that both instruments independently see the same variations of ozone at this altitude. Figure 5 shows a sample measurement of the diurnal variations of ozone averaged over a two week period in the winter of 1990. Studies of the diurnal data are ongoing.

## Publications

Parrish, A., Connor, B. J., and Tsou, J. J., Ground-based microwave monitoring of stratospheric ozone, submitted to Geophysical Research Letters, 1991.



## A. TESTING AND OPERATION OF MILLIMETER WAVE ClO RECEIVERS FOR THE NETWORK FOR THE DETECTION OF STRATOSPHERIC CHANGE

Grant No. NAGW-1560

## B. PRINCIPAL INVSTIGATOR

Philip Solomon,  
State University of New York  
Stony Brook, NY 11794

## C. ABSTRACT

The objectives of this research are to test and operate new ground-based instruments measuring chlorine oxide (ClO) in the stratosphere. The first new millimeter wave receiver will be operated from a site at the 14,000 foot level on Mauna Kea, Hawaii. Chlorine oxide is the principal chemical involved directly in the depletion of ozone resulting from the atmospheric release of man-made chlorofluorocarbons. Our goals are to characterize the current concentration and altitude distribution of stratospheric chlorine oxide, and to determine the secular changes in the chlorine oxide distribution over a period of at least 10 years. The first three ClO instruments built as part of the Network for the Detection of Stratospheric Change (NDSC) will all be tested at this site, and one of them will be operated at this site on a long-term basis.

## D. SUMMARY OF PROGRESS AND RESULTS

During 1990 and the first half of 1991, we have been preparing the site by modifying laboratory space on top of Mauna Kea in order to operate the new millimeter-wave ClO receivers in an automatic mode. The first two new instruments will be tested at this site during September-October, 1991. Ongoing work has included software development and the establishment of communication lines for remote control and data acquisition. We have also been developing algorithms for interpretation of the data and retrieval of altitude distributions from the observed spectral lines. The new instruments constructed by the Millitech Corporation are ready for testing as of August, 1991, and the final work on our site should be completed as of September, 1991. A complete review of our technique and past successful measurements of ClO in the stratosphere has been carried out in preparation for comparison with our new measurements to determine stratospheric change.

## E. PUBLICATION

P. M. Solomon and J. W. Barrett, "From Hawaii to the Antarctic Ozone Hole: Millimeter-Wave Observations of Chlorine and Depletion of the Ozone Layer" in *Proceedings of Workshop on Coherent Detection at Millimeter Wavelengths and Their Applications*, Nova Science Publishers, 1991.

Title: Ground-Based Microwave Instrument for Monitoring  
Stratospheric Chlorine Monoxide

Principal Investigator: A. Parrish  
Millitech Corp.

Co-investigators: B. J. Connor  
NASA Langley Research Center

P. M. Solomon  
State University of New York  
at Stony Brook

#### Abstract of Research Objectives:

The objective of this work is to develop a microwave instrument for long term monitoring of stratospheric chlorine monoxide, and to construct two such instruments for use in the Network for Detection of Stratospheric Change. (The Chemical Manufacturers Association has separately funded the construction of a third instrument, also for use in the Network). These ground based instruments will measure the rotational transition of ClO in emission at 278.63 GHz. They are intended for monitoring the long term secular trend in ClO expected from continuing deposition of chloroflourocarbons in the environment; so maintenance of absolute instrument calibration over a period of a decade is important. The instruments are designed for automated operation at remote sites with data downloaded to a central computer for processing.

#### Summary of Progress and Results:

The the first instrument was assembled in prototype form and placed into operation at the Millitech facility at the end of January, 1991. A severe baseline artifact was observed in the spectra; this was traced to the dewar window, which was modified. ClO observations were then made at nearly every opportunity allowed by the weather (suitable dry weather occurs only occasionally in the winter and early spring at the Millitech location). Eight ClO observations were made after February 15th, after the dewar window was modified. Three of these are of very good quality; the remaining five contain low level spectral artifacts. Further modifications were made to reduce the artifacts at the end of April when first instrument was completed in deliverable form at the end of April. Manufacturing of the second instrument was completed at the end of June. The third (CMA funded) instrument is 95% complete. Intercomparisons of the two completed instruments at Mauna Kea are planned for September.

Publications: None to date



RESEARCH SUMMARY FOR  
NASA UPPER ATMOSPHERE RESEARCH PROGRAM

1 SEPTEMBER 1991

A. TITLE:

Microwave Measurements of Stratospheric and Mesospheric Water Vapor

B. INVESTIGATORS/INSTITUTIONS:

Dr. Charles L. Croskey  
Dr. John J. Olivero  
Communications and Space Sciences Laboratory  
316 Electrical Engineering East  
Department of Electrical and Computer Engineering  
The Pennsylvania State University  
University Park, PA 16802

C. ABSTRACT OF RESEARCH OBJECTIVES:

This is a program built around the observation and analysis of water vapor within the middle atmosphere (the stratosphere and mesosphere). Much of the chemistry of the middle atmosphere depends directly upon the water vapor concentration at these levels. Photodissociation of water vapor by solar radiation above 70 km is a major sink; it is balanced by upward diffusion from below. The atomic hydrogen resulting from the photodissociation escapes into the exosphere and is a major loss term in the Earth's hydrogen budget. Photochemical models of the ozone in the upper stratosphere and mesosphere show a strong dependence on the H<sub>2</sub>O photolysis products (HO<sub>x</sub>). Water vapor also serves as a tracer of atmospheric transport. In the lower ionosphere, H<sub>2</sub>O controls the formation of cluster ions, whose chemistry influences electron densities and hence radiowave propagation in the region. Finally, the formation of Polar Stratospheric Clouds and Polar Mesospheric Clouds (Noctilucent Clouds) also depend critically upon middle atmospheric H<sub>2</sub>O.

Water vapor measurements by ground-based microwave radiometry have been conducted from the University Park Campus (central PA) of Penn State University for nearly a decade and continue as the first dedicated facility of its kind. A second radiometer extends these measurements both to other locations and down to lower levels in the stratosphere. The observations of stratospheric and mesospheric water vapor made by the second, portable radiometer serve two major scientific programs: these measurements will be a part of the UARS Correlative Measurements Program and they will also contribute to the Network for the Detection of Stratospheric Change.

#### D. SUMMARY OF PROGRESS AND RESULTS:

We continue to extend the H<sub>2</sub>O data set at the central Pennsylvania site through routine observations. Operations have been confined to the late fall through early spring time periods when conditions are most favorable. We are continuing to develop off-line signal processing software to reduce operator intervention and speed data analysis.

The major task in the most recent period of work has been the design and construction of the new, portable radiometer system for the ground-based microwave measurement of water vapor from many possible sites. The design was driven by several, sometimes conflicting goals. To make these measurements the radiometer must be sensitive, stable, and well calibrated to maximize the measurement signal-to-noise ratio. At the same time we have designed the portable radiometer so that it can be air-freighted from one location to another and withstand the rigors of such shipments.

The current instrument design features the following: a motor-driven, planar reflector which directs the atmospheric emissions into the fixed, circular horn antenna at predetermined elevation angles; the signal is amplified by a cooled HEMT pre-amplifier to reduce the receiver noise temperature; a reference signal is injected during half of each measurement cycle to calibrate the receiver; absolute calibration is achieved using a liquid nitrogen cold load as needed; and the spectral line analysis is accomplished using a variably-spaced filter bank.

Transportability of the radiometer system is achieved by building it as a series of modules, each in its own shipping container/enclosure. Shock-mounting and padding are used extensively to isolate the electronic components from transportation loads.

#### E. JOURNAL PUBLICATIONS:

1. "The Seasonal Variation of Water Vapor and Ozone in the Upper Mesosphere: Implications for Vertical Transport and Ozone Photochemistry", R.M. Bevilacqua, D.F. Strobel, M.E. Summers, J.J. Olivero, and M. Allen, Journal of Geophysical Research, 95, 883-893, 1990.
2. "Radiometric Remote Sensing of Mesospheric and Stratospheric Water Vapor", C.L. Croskey, J.J. Olivero, and J.P. Martone, IGARSS '91 Conference Proceedings, June, 1991.
3. "Ground-Based Microwave Remote Sensing of Water Vapor in the Mesosphere and Stratosphere", C.L. Croskey, J.J. Olivero, and J.P. Martone, SPIE Proceedings on Remote Sensing of Atmospheric Chemistry, vol. 1491, pp. 39, 1991.

A. Title: Ground-based Monitoring of Water Vapor in the Earth's Middle Atmosphere

B. Investigators: R.M. Bevilacqua. P.R. Schwartz, W.B. Waltman, and  
T.A. Pauls

Center for Advanced Space Sensing  
Naval Research Laboratory  
Washington, DC 20375-5000

D. L. Thacker  
Interferometrics Inc.  
Vienna, VA 22180

C. Abstract of Research Objectives:

The primary objective is to construct, test, and operate in the field a ground-based mm-wave instrument for measuring the water vapor mixing ratio profile in the middle atmosphere on a routine and continuous basis. This instrument will serve as the prototype for a series of such instruments projected to be part of the Network for Detection of Stratospheric Change. The design goals of the instrument are as follows:

- (1) Simultaneous measurements in the 20-75 km altitude range
- (2) Good long-term relative precision
- (3) Capable of semi-automatic operation at a remote field site.

The instrument is based on a state-of-the-art high electron mobility transistor (HEMT) amplifier, which provides sufficiently large RF bandwidth in order to measure water vapor into the lower stratosphere. The instrument spectrometer is a prototype of the unit designed and built for the Millimeter-wave Atmospheric Sounder (MAS) shuttle experiment.

D. Summary of Progress and Results:

In January, 1991 tests of the instrument were completed and it was shipped to the Maryland Point (radio astronomy) Observatory for an initial field site experiment. The purpose of this experiment was to evaluate the instrument performance, especially baseline structure and stability, and to investigate the suitability of the instrument for remote operation. The results from the Maryland Point field site experiment were, in general, quite good. Spectral measurements obtained at Maryland Point have been inverted to yield the water vapor mixing ratio profile in the 35 to 75 km region. (Residual instrumental baseline structure in the line wings prevented the measurements from being extended down to 20 km). The results are in good agreement with both our previous measurements, and with recent space-based measurements. Thus, we regard these initial measurements as verifying both the instrument concept and suitability for automatic operation.

In late June 1991 the instrument was installed at the JPL Table Mountain Observatory in California to begin a long series of measurements at a high altitude dry site in order to completely evaluate instrument performance. The installation of the instrument went well and we have been making routine water vapor measurements (in the 35-75 km region) at TMO since about 1 July 1991. Attention has now focused on improving the baseline structure in the wide bandwidth channels to extend the water vapor measurements down to 20 km

and, thereby, exploit the full capability of the instrument. In addition, at TMO, we plan to perform a complete data validation study using predominantly SAGE II measurements. Finally, we plan to participate in photochemical studies using the water vapor measurements in conjunction with measurements of other important middle atmospheric parameters most notably ozone which is also measured routinely at TMO both by lidar and by mm-wave techniques. In late summer, 1992 the instrument will be shipped to the first NDSC field site at Mauna Loa.

**E. Publications:**

Bevilacqua, R.M., P.R. Schwartz, T.A. Pauls, W.B. Waltman, and D.L. Thacker, Ground-based monitoring of water vapor in the middle atmosphere: the NRL water vapor millimeter-wave spectrometer, Proceedings of SPIE Conference 1491, Remote Sensing of Atmospheric Chemistry, Society of Photo-Optical Instrumentation Engineers, Bellingham, Washington, 1991.

A. Title of Research:

Retrieval Methods for Ground-based Millimeter-Wave Measurements  
for the Network for the Detection of Stratospheric Change

B. Investigators and Institutions:

Co-Principal Investigators:

Brian J. Connor  
Atmospheric Sciences Division  
NASA Langley Research Center  
Hampton, VA

Richard M. Bevilacqua  
Center for Advanced Space Sensing  
Naval Research Laboratory  
Washington, DC

C. Abstract of Research Objectives:

The fundamental objective is to determine the information available in ground-based millimeter-wave measurements of stratospheric constituent profiles, to identify the optimum method of retrieving this profile information, and to characterize the errors in the final result. A secondary objective is to produce retrieval software for operational use with Network for the Detection of Stratospheric Change (NDSC) measurements of  $O_3$ ,  $H_2O$ ,  $ClO$ , and perhaps  $N_2O$ .

D. Progress and Results:

The millimeter-wave forward model, called Millimeter-wave Emission Temperature of the Atmosphere (META), has been validated by comparison with pre-existing, less general models at both NASA Langley and at the Naval Research Laboratory. Driver programs have been written to perform retrievals and to calculate the measurement contribution functions as part of a complete error analysis. Three different retrieval modules, which can be used interchangeably by the drivers, have been written, employing the optimal estimation, Chahine, and Backus-Gilbert methods. A comparative study of the three algorithms is underway.

The interfaces among the various software modules have been kept simple and generic, to allow their application to other experiments. In particular the error analysis drivers and retrieval modules have been written so as to be applicable to virtually any remote sensing problem. The optimal estimation module has been successfully applied, in an experimental mode, to infrared Fourier Transform Spectroscopic measurements. We are currently considering application of the software to ground-based lidar measurements of ozone.

Finally, a complete error analysis of the NDSC microwave ozone measurements was carried out. This shows the measurement precision to be 4-6% and accuracy to be 4-8% between 20-60 km. Measurement vertical resolution is 8-10 km between 20-40 km and increases to 15 km at 60 km.

E. Publications:

Connor, B.J., A. Parrish, and J.J. Tsou, "Detection of Stratospheric Ozone Trends by Ground-based Microwave Observations," Proceedings of SPIE Conference 1491, Remote Sensing of Atmospheric Chemistry, Society of Photo-Optical Instrumentation Engineers, Bellingham, Washington, 1991.



D. AIRCRAFT-BORNE MEASUREMENTS

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A. Title of Research Task

Aircraft Mission Meteorological Support and Data Management

B. Investigators and Institutions

R. Stephen Hipskind, NASA/Ames Research Center  
Steven E. Gaines, Sterling Software

C. Research Objectives

Establish a facility for obtaining meteorological data to support aircraft field campaigns and other research projects. Provide data management for aircraft field campaigns.

D. Progress and Results

Meteorological Support

A Meteorological Satellite Downlink and Display System (MSDDS) was recently acquired which receives and displays the direct digital imagery from both geostationary and polar orbiting meteorological satellites. The MSDDS is a portable system which can be shipped and set up to receive satellite imagery virtually anywhere in the world. Its primary purpose is in support of large aircraft field operations for which access to real time cloud imagery is critically important. We have also put in place a joint agreement with Goddard Space Flight Center and the National Meteorological Center (NMC) to obtain via the NASA Science Internet (NSI) network the NMC forecast and analysis fields, as well as other pertinent meteorological data available from the NMC, in support of NASA field campaigns and research projects.

Field Campaign Data Management

Our group has taken the responsibility for archiving and distributing the data from the polar ozone field campaigns. This has been accomplished by publishing the field datasets on CDROM. Published in 1990 were two discs - the aircraft and related data for the 1989 Airborne Arctic Stratospheric Expedition (AASE), NASA/UARP-003, and a separate disc with the 5 Hz Meteorological Measurement System data from the 1989 AASE ER-2 flights, published as Appendix A to NASA/UARP-003. To improve on the actual exchange of the aircraft data during the field experiments we have purchased Local Area Networking (LAN) equipment which will be set up at the remote deployment locations. All aircraft and science team Principal Investigators (PI's) will be tied together via the LAN in the field. The LAN will in turn be tied to a wide-area connection into the NASA Internet, providing access to mission critical datasets from external sources, (meteorological forecasts, for example), as well as access to PI's home labs. The aircraft data from the individual instruments will be submitted to a central archive computer in the field via the LAN. The LAN and Internet connectivity will be installed for the upcoming AASE II field campaign based in Bangor, Maine from October, 1991 through March, 1992.

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## Meteorological Measurements System

PI: Paul A. Newman  
Code 916  
NASA/GSFC  
Greenbelt, MD 20771

CoI: Steve Hipskind  
Code SGA  
NASA/Ames  
Moffett Field, CA 94035

The Meteorological Measurements System is a computer workstation dedicated to processing near real-time meteorological data, and providing that data to aircraft campaigns. A Silicon Graphics 4D/35 workstation was procured in late 1990 for this task. The system has been installed on the network, and software has been developed for automatically transferring, processing, and archiving the meteorological data. Three basic types of information are currently set up for transfer: radiosondes, meteorological analyses, and forecast data. This system will be fully available for use during the Airborne Arctic Stratospheric Expedition II.

## **Stratosphere-Troposphere Exchange Project Management**

Philip B. Russell (Project Manager)  
and Leonhard Pfister (Project Scientist)  
NASA/Ames Research Center

### **Research Objectives**

This task provides management and related support for the Stratosphere-Troposphere Exchange Project (STEP). STEP's overall goal is to better understand the processes by which man-made and natural chemicals are transported into the stratosphere and, once there, to the ozone layer. Because any exchange process must be consistent with the very low relative humidities observed in the lower stratosphere, STEP also emphasizes the study of mechanisms that could dehydrate air entering the stratosphere. STEP has addressed these goals by conducting three major field campaigns: two midlatitude field experiments in Spring of 1984 and Spring of 1986, and a tropical field experiment in Austral summer (January-February) of 1987. The objective of the midlatitude experiments was to identify modes of transport during large-scale cyclogenesis, both (1) within the stratosphere, from the anticyclonic to the cyclonic side of the jet, and (2) from the troposphere to the stratosphere. The objective of the STEP Tropical Experiment was to improve understanding of exchange and dehydration processes in the tropics, with particular emphasis on processes associated with tropical cumulonimbus clouds.

### **Summary of Progress and Results**

In 1990-91 this task focused on analysis and dissemination of results from the STEP field campaigns. A two-day science team meeting was held in April, 1990 to discuss progress on data analysis; an informal report on that meeting is available from the project scientist.

A special section of *J. Geophys. Res.* devoted to the STEP 1984 experiment was completed during 1991 and is scheduled for publication in late CY 1991. The section includes an overview paper and a preface written specifically under this research task (see Publications, below). These and the remaining four papers have all undergone final revisions, acceptance, and galley proofing. At this writing a special color cover illustration has been submitted to *J. Geophys. Res.* and is being readied by them.

The 1986 field experiment was the smallest of the three STEP field programs, and data analysis (and even data reduction) has been held up by the rush of other aircraft field programs since that time. Work is just beginning on the five science flights for the STEP 1986 field program. The project scientist has gathered essential ancillary meteorological data, and has been gathering the aircraft measurements to begin analysis.

A special section of *J. Geophys. Res.* on the 1987 STEP tropical experiment was also organized in 1990-91. About 12 papers are planned. Of these, the overview paper and one contributed paper have been submitted to the journal for peer review, three contributed papers have been circulated among the science team, and the remainder are in various stages of preparation.

*Biennial Research Summary, 1990-91*  
*Upper Atmosphere Research Program, Aircraft-Borne Measurements*

**Publications**

- Russell, P. B., E. F. Danielsen, R. A. Craig, and H. B. Selkirk, 1991: The NASA Spring 1984 stratosphere-troposphere exchange experiments: science objectives and operations. *J. Geophys. Res.*, in press.
- Pfister, L., P. B. Russell, E. F. Danielsen, and R. T. Watson, 1991: Preface [to above special issue]. *J. Geophys. Res.*, in press.
- Russell, P. B., L. Pfister, and H. B. Selkirk, 1991: The tropical experiment of the Stratosphere-Troposphere Exchange Project (STEP); science objectives and operations. *J. Geophys. Res.*, submitted.

## **BIENNIAL RESEARCH SUMMARY**

- A. TASK # 464-14-03-10 AIRCRAFT DEPLOYMENT**  
**TASK # 464-14-05-10 POLAR OZONE PROJECT MANAGEMENT**

### **B. INVESTIGATORS AND INSTITUTIONS**

Project Manager Estelle Condon, Earth Systems Science Division  
Ames Research Center, Moffett Field, CA.  
Deputy Manager Steve Hipskind, Earth Systems Science Division  
Ames Research Center, Moffett Field, CA.  
Science Coordinator Brian Toon, Earth Systems Science Division  
Ames Research Center, Moffett Field, CA.  
Science Coordinator Steve Wegener, Earth Systems Science division  
Ames Research Center, Moffett Field, CA.  
AASE Project Scientist Adrian Tuck, NOAA Aeronomy Laboratory  
Boulder, CO.  
AASE II Project Scientist James Anderson, Harvard University  
Cambridge, MA.

### **C. RESEARCH OBJECTIVES**

The Polar Ozone Experiments conducted in 1987 from Punta Arenas, Chile and in 1989 from Stavanger, Norway had as their primary objective to study the production and loss mechanisms of ozone in the Earth's polar stratosphere. The investigations were undertaken to study the effect on ozone distribution of the Antarctic and Arctic Polar vortices and of the cold temperatures associated with the formation of Polar Stratospheric Clouds (PSC's).

### **D. SUMMARY OF PROGRESS AND RESULTS**

Efforts during this period were directed toward publication of a special journal issue, Geophysical Research Letters, March Supplement 1990, describing the results of the Airborne Arctic Stratospheric Expedition and the release on CDROM of the complete data archive.

Planning for the Airborne Arctic Stratospheric Expedition II was accomplished: platforms and payloads were selected and the operational sites for the experiment were chosen (Fairbanks, Alaska and Bangor Maine). Initial work for implementation of the AASE II was begun with the site preparation in Bangor.

### **E. PUBLICATIONS**

Geophysical Research Letters, 17, 313-564, March Supplement 1990. Special Issue.

Journal of Geophysical Research, Polar Ozone Special Issue, December 1991.

A. Title:

DC-8 Mission Planning (Task 464-14-06-10)

B. Investigators and Institutions:

Dr. Owen B. Toon, Earth System Science Division, NASA Ames Research Center, Moffett Field, Ca. 94035

C. Objective:

The objective of this project is to provide science guidance for the operation of the DC-8 aircraft in field programs and to aid DC-8 investigators in the interpretation of their data.

D. Progress and Results:

The DC-8 aircraft was successfully operated during the deployment phase of the Arctic Ozone Expedition in January and February of 1989. Lidar data collected by one of the investigators revealed the presence of two types of extensive systems of polar stratospheric clouds of varying backscattering properties. An analysis of these data, conducted under this task, suggests that particle size differences, caused by variations in atmospheric cooling rate, were responsible for creating the two classes of nitric acid containing clouds observed by the lidar.

A number of tasks were performed to prepare to operate the DC-8 aircraft in the Airborne Arctic Ozone Expedition II/High Speed Research Program Mission planned for October, 1991 through March 1992. These tasks include development of improved navigational computer programs and advanced planning for flight tracks. The calendar for this complex mission, details of the scientific components of the mission and the science goals of the mission were defined in conjunction with other scientists and program managers involved with this project. Computer graphical packages are being developed so that data collected during the expedition are quickly available to the entire science team.

E. Publications:

O. B. Toon, E. V. Browell, S. Kinne, and J. Jordan, An analysis of lidar observations of polar stratospheric clouds, Geophys. Res. Lett., 17, 393-396, 1990.

## NASA Upper Atmosphere Research Program: Research Summary 1990-91

### A. Title of Research Task

The ER-2 Meteorological Measurement System (MMS)

### B. Principal Investigator and Institution

K. Roland Chan  
NASA, Ames Research Center  
M.S. 245-5  
Moffett Field, CA 94035-1000

### C. Abstract of Research Objectives

The objectives of ER-2 MMS are (a) to measure the meteorological parameters - temperature, pressure, and the wind vector - accurately, (b) to provide high-resolution data of atmospheric state variables and aircraft flight track to investigators on a timely basis, and (c) to conduct collaborative research in atmospheric dynamics and chemistry.

### D. Summary of Progress and Results

1. Modified hardware and software to provide telemetry downlink and real-time capability.
2. Demonstrated successfully the real-time wind computational capability in October, 1990.
3. Reprocessed MMS data (1-Hz & 5-Hz) of the STEP, AAOE, and AASE I missions.
4. Processed MMS data of the 1986 STEP science flights for the first time.
5. Analyzed mesoscale wave phenomena observed in STEP, AAOE and AASE I.
6. Participated in the "water intercomparison" flight series in February, 1991.
7. Calibrated the MMS instrumentation with the ER-2 [NASA 709] aircraft for the first time.
8. Conducted a feasibility study of relocating the MMS radome differential pressure system.
9. Participated in the test flights in preparation for the AASE II mission.

### E. Journal Publications

- Chan, K.R., S.W. Bowen, S.G. Scott, and T.P. Bui, The NASA ER-2 MMS: instrumentation, calibration and intercomparison results, *Rpt. of the Intl Workshop on the Airborne Measurement of Wind, Turbulence and Position*, July 26-28, 1989, Oberpfaffenhofen, Germany, edited by H.P. Fimpel, D. Baumgardner, and A.M. Jochum, 51-55, 1990.
- Scott S.G., T.P. Bui, K.R. Chan, and S.W. Bowen, The Meteorological Measurement System on the NASA ER-2 Aircraft, *J. Atmo. and Oceanic Tech*, 7, 525-540, 1990.
- Fahey, D.W., K.K. Kelly, S.R. Kawa, A.F. Tuck, M. Loewenstein, K.R. Chan, and L.E. Heidt, Observation of denitrification and dehydration in the winter polar stratosphere, *Nature*, 344, 321-324, 1990.
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- Dye, J.E., B.W. Gandrud, D. Baumgardner, K.R. Chan, G.V. Ferry, M. Loewenstein, Observed particle evolution in the polar stratospheric cloud of January 24, 1989, *Geophys. Res. Lett.*, 17, 413-416, 1990.
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- Schoeberl, M.R., M.H. Proffitt, K.K. Kelly, L.R. Lait, P.A. Newman, J.E. Rosenfield, M. Loewenstein, J.R. Podolske, S.E. Strahan, and K.R. Chan, Stratospheric constituent trends from ER-2 profile data, *Geophys. Res. Lett.*, 17, 469-472, 1990.

- Rood, R.B., P.A. Newman, L.R. Lait, D.J. Lamich, and K.R. Chan, Stratospheric temperatures during AASE: results from STRATAN, *Geophys. Res. Lett.*, 17, 337-340, 1990.
- Loewenstein, M., J.R. Podolske, K.R. Chan, and S.E. Strahan, N<sub>2</sub>O as a dynamical tracer in the Arctic vortex, *Geophys. Res. Lett.*, 17, 477-480, 1990.
- Kawa, S.R., D.W. Fahey, L.C. Anderson, M. Loewenstein, and K.R. Chan, Measurement of total reactive nitrogen during the AASE, *Geophys. Res. Lett.*, 17, 485-488, 1990.
- Fahey, D.W., S.R. Kawa, and K.R. Chan, Nitric Oxide Measurements in the Arctic winter Stratosphere, *Geophys. Res. Lett.*, 17, 489-492, 1990.
- Brune, W.H., D.W. Toohey, J.G. Anderson, and K.R. Chan, In situ observations of ClO in the Arctic Stratosphere: ER-2 aircraft results from 59°N to 80°N latitude, *Geophys. Res. Lett.*, 17, 505-508, 1990.
- Toohey, D.W., J.G. Anderson, W.H. Brune, and K.R. Chan, In situ observations of BrO in the Arctic Stratosphere, *Geophys. Res. Lett.*, 17, 513-516, 1990.
- Lait, L.R., M.R. Schoeberl, P.A. Newman, M.H. Proffitt, M. Loewenstein, J.R. Podolske, S.E. Strahan, K.R. Chan, B. Gary, J.J. Margitan, E. Browell, M.P. McCormick, and A. Torres, Reconstruction of O<sub>3</sub> and N<sub>2</sub>O fields from ER-2, DC-8, and balloon observations, *Geophys. Res. Lett.*, 17, 521-524, 1990.
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- Salawitch, R.J., M.B. McElroy, J.H. Yatteau, S.C. Wofsy, M.R. Schoeberl, L.R. Lait, P.A. Newman, K.R. Chan, M. Loewenstein, J.R. Podolske, S.E. Strahan, and M.H. Proffitt, Loss of ozone in the polar vortex for the winter of 1989, *Geophys. Res. Lett.*, 17, 561-564, 1990.
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- Kawa, S.R., D.W. Fahey, S. Solomon, W.H. Brune, M.H. Proffitt, J.G. Anderson, L.C. Anderson, and K.R. Chan, Interpretation of aircraft measurements of NO, ClO, and O<sub>3</sub> in the lower stratosphere, *J. Geophys. Res.*, 95, 18597-18609, 1990.
- Chan, K.R., S.G. Scott, S.W. Bowen, S.E. Gaines, E.F. Danielsen, and L. Pfister, Horizontal wind fluctuations in the stratosphere during large scale cyclogenesis, in press, *J. Geophys. Res.*, 1991.
- Toohey, D.W., W.H. Brune, K.R. Chan, and J. G. Anderson, In situ measurements of mid-latitude ClO in winter, *Geophys. Res. Lett.*, 18, 21-24, 1991.
- Gaines, S. E., S. W. Bowen, R. S. Hipskind, T. P. Bui, and K. R. Chan, Comparisons of the NASA ER-2 MMS with radar tracking and radiosonde data, submitted to *J. Atmo. and Oceanic Tech.*, 1991.
- Chan, K.R., L. Pfister, T.P. Bui, S.W. Bowen, and J. Dean-Day, Applications of the ER-2 MMS, *Fourth Airborne Geoscience Workshop*, La Jolla, Calif., Jan. 29 to Feb. 1, 1991.
- Bowen, S.W., K.R. Chan, T.P. Bui, The Calibration of the ER-2 MMS, *Fourth Airborne Geoscience Workshop*, La Jolla, Calif., Jan. 29 to Feb. 1, 1991.
- Wilson, J.C., M.R. Stolzenburg, W.E. Clark, M. Loewenstein, G.V. Ferry, K.R. Chan, S.R. Kawa, and K.K. Kelly, Stratospheric sulfate aerosol in and near the northern hemisphere polar vortex: The morphology of the sulfate layer, multimodal size distribution and the effect of denitrification, submitted to *J. Geophys. Res.*, 1991.



*Research Summaries FY 1990-91: Upper Atmosphere Research Program,  
Aircraft-Borne Measurements*

- A. Stratospheric N<sub>2</sub>O Measurements with ATLAS, the Airborne Tunable Laser Absorption Spectrometer**
- B. Dr. Max Loewenstein and Dr. James R. Podolske, NASA/Ames Research Center**
- C. Dr. Susan E. Strahan (collaborating scientist) NOAA Geophysical Fluid Dynamics Laboratory, Princeton University, Princeton, NJ**
- D. Research Objectives**

Our main current objective with the ATLAS instrument is to carry out high time and space resolution N<sub>2</sub>O tracer measurements, especially in and near the winter polar vortex. This work directly supports the ongoing investigation of heterogeneous chlorine chemistry believed to be responsible for the Antarctic ozone depletion observed in austral spring. Correlations of N<sub>2</sub>O with NO<sub>y</sub> (total reactive nitrogen) and of N<sub>2</sub>O with O<sub>3</sub> provide information on the atmospheric chemical state. Deviations from normal correlations indicate perturbed atmospheric conditions due, for example, to heterogeneous chemistry on polar stratospheric clouds (PSCs) and photochemical loss of ozone. N<sub>2</sub>O measurements also identify regions of strong diabatic cooling and provide the data to quantify atmospheric subsidence in these regions.

**E. Summary of Progress and Results**

Analysis and final calibration and archiving of all AASE (Airborne Arctic Stratospheric Expedition) data was completed during the period covered by this report (Loewenstein et al., 1990a, 1990b). A study of the correlation of N<sub>2</sub>O with NO<sub>y</sub> was undertaken in cooperation with the NOAA investigators responsible for the NO<sub>y</sub> measurements. A persistent linear correlation of N<sub>2</sub>O versus NO<sub>y</sub> has been observed during both AASE and AAOE (Airborne Antarctic Ozone Experiment) when observations only outside the polar vortex are considered. In a study published in *Nature* (Fahey et al., 1990) we examined the theoretical basis of this correlation using a two dimensional atmospheric photochemical model. As a result of this work we believe that the main features of the N<sub>2</sub>O/NO<sub>y</sub> correlation are understood. It is now possible to use observed deviations from this normal correlation to identify and quantify disturbed chemical conditions in the atmosphere. These disturbed conditions have so far been observed only inside or near the boundary of the polar vortex (both northern and southern winter hemispheres) and are believed to arise from heterogeneous

chemistry on nitrate aerosols (PSCs). We will continue to look for evidence of disturbed chemical conditions caused, as well, by normal mid-latitude or tropical sulfate aerosol, or from enhanced sulfate aerosol arising from volcanic eruptions such as the recent, large Pinatubo sulfur injection into the stratosphere.

For mid-latitude winter conditions a linear correlation of  $\text{N}_2\text{O}$  and ozone is also observed in the AASE data. Inside the Arctic vortex this linear relationship tends to break down, especially for the higher values of potential temperature. These observations have tentatively been ascribed to photochemical destruction of ozone inside the Arctic vortex (Proffitt et al. 1990). Research is continuing to place these observations and interpretations on a firmer experimental and theoretical footing.

Our recent work has focused on preparations for the AASE II campaign which will take us into the Arctic vortex during the period October 1991 through March 1992 to observe both the setup and breakdown of the vortex, as well as its fully evolved state. Test flights being carried out in August and September 1991 in preparation for AASE II provide us with an opportunity to refine and improve instrument operation. Improvements in instrument calibration and streamlining of some of our data analysis techniques has been an additional intensive focus of recent work.

## **F. Publications**

Fahey, D. W., S. Solomon, S. R. Kawa, M. Loewenstein, J. R. Podolske, S. E. Strahan, and K. R. Chan, A diagnostic for denitrification in the winter polar stratospheres, *Nature*, 345, 698, 1990.

Loewenstein, M., J. R. Podolske, K. R. Chan, and S. E. Strahan,  $\text{N}_2\text{O}$  as a dynamical tracer in the Arctic vortex, *Geophys. Res. Lett.*, 17, 477, 1990a.

Loewenstein, M., J. R. Podolske, and S. E. Strahan, ATLAS instrument characterization: Accuracy of the AASE and AAOE nitrous oxide datasets, *Geophys. Res. Lett.*, 17, 481, 1990b.

Proffitt, M. H., J. J. Margitan, K. K. Kelly, M. Loewenstein, J. R. Podolske, and K. R. Chan, Ozone loss in the Arctic polar vortex inferred from high-altitude aircraft measurements, *Nature*, 347, 31, 1990.

**A. Ames ER-2 Ozone Measurements**

**B. Dr. Richard Pearson, Jr., NASA/Ames Research Center**

**C. (no Co-Investigators)**

**D. Research Objectives**

The primary objective of this work is to support the measurement of the mixing ratio of Ozone throughout the lower stratosphere using the Ames Ultraviolet Ozone Photometer (UOP) on NASA high altitude ER-2 aircraft, especially in the region of ozone depletion near the winter polar vortex. Additional objectives are to investigate the feasibility of using telemetry to obtain ozone data from the ER-2 in near real time during actual aircraft flights, and to maintain the UOP in operational status when it is not used for major campaigns.

**E. Summary of Progress and Results**

During the past two years, this instrument has been a backup instrument for the major NASA stratospheric deployments such as the Airborne Arctic Stratospheric Expedition. In order to maintain its operational status, we have flown it on missions such as the Telescience flights during November, 1990. We obtained valid ozone data from both through the telemetry link, and from the on-board computer in the instrument. This data is being analyzed and prepared for publication. We will continue to fly the UOP in the future to validate its operational status, subject to the availability of flight hours. We have also continued to test the instrument in the lab to ensure that it is operating satisfactorily.

Many of the stratospheric chemistry flights have been assigned to a different ER-2 platform than used previously, and the new platform lacked the special mounting hole in the fuselage for the UOP sample inlet which severely limited our possibilities for flights for the instrument. The hatch of this aircraft has been modified to accept the UOP sample inlet so that UOP can be flown in future missions.

**F. Publications**

(None in 1990-1)

## **Support of the Harvard ClO/BrO Instrument for the Preparation, Execution, and Data Review for the Arctic Vortex Mission**

### **Investigator and Institution:**

William H. Brune  
Department of Meteorology  
Pennsylvania State University  
University Park, PA 16802

### **Abstract**

Two chemical species that are intimately involved in the destruction of ozone in the lower stratosphere are ClO and BrO. In this work, we used the Harvard University ClO/BrO instrument, mounted on the NASA ER-2 high altitude aircraft, to study the abundances of these species in the Northern Hemisphere, particularly near the Arctic polar vortex in 1989. The scientific objectives were to understand the response of the chemical species to the changing environment of the wintertime polar stratosphere, and the potential effects that these changes in ClO and BrO abundances have on other species, particularly ozone.

### **Summary of Progress and Results**

The successful Airborne Arctic Stratospheric Experiment and its associated test flights yielded excellent data on a number of chemical species, and ClO and BrO were no exceptions. Several analyses of these data, for a variety of issues, have been completed and published during the last two years.

Perhaps the most important result was that the ClO abundances in the Arctic polar vortex were as large as those observed in the Antarctic ozone hole, with observed values exceeding 1.2 ppbv. Enhanced levels of ClO were observed in early January, two months before the Spring equinox. Furthermore, calculations assuming thermal equilibrium between ClO and Cl<sub>2</sub>O<sub>2</sub> in the dark polar stratosphere indicate that most, if not all, of the available, inorganic chlorine had been shifted to ClO and Cl<sub>2</sub>O<sub>2</sub> from HCl and ClONO<sub>2</sub> by mid-January between the potential temperatures of 390 K and 470 K. Thus the heterogeneous processes that convert chlorine to reactive forms were efficient enough in 1989 that the conversion was essentially complete in early winter. As a result, enhanced amounts of ClO, capable in sunlight of the rapid destruction of ozone, were available in early winter and remained available into mid-February.

The BrO mixing ratios in the Arctic polar vortex were measured to be  $8 \pm 2$  pptv, about twice the levels measured outside the vortex. These values in the Arctic chemically perturbed region were comparable to those measured in the Antarctic chemically perturbed region.

A modeling study that we performed showed that once the chlorine, bromine, and reactive nitrogen families have been thoroughly altered by the presence of PSCs, the destruction of 10% to 15% of the ozone in that air mass is virtually assured. Taken over the depth of the chemically perturbed region, this loss translates into a 5% to 8% loss in column ozone. This study also indicated that the time constant for ozone destruction in the Arctic polar vortex will decrease sufficiently in the future, as the chlorine abundance of the stratosphere increases, that large reduction of Arctic ozone, although somewhat unlikely at present, will become increasingly more likely.

Other studies were focused on the chemistry that might be occurring outside the Arctic polar vortex. A comparison was made between ClO data obtained outside the Arctic polar vortex and the results of calculations that included conversion chemistry on background sulfuric acid aerosols. The conclusion was that conversion of the chlorine from reservoir to reactive forms was inefficient on the global background sulfate aerosol layer at temperatures above the PSC formation temperature. This result was in agreement with the expectations from recent laboratory experiments. In a second study, ClO mixing ratios measured outside the Arctic polar vortex were found to be 150 pptv, the largest amounts ever measured at midlatitudes. Although these large values appeared to be associated with the heterogeneous chemistry inside the polar vortex, the seasonal trend of midlatitude ClO mixing ratios suggests that other chemistry in the midlatitudes may be occurring.

### Journal Publications

- Brune, W. H., D. W. Toohey, J. G. Anderson, and K. R. Chan, In situ observations of ClO in the Arctic Stratosphere: ER-2 aircraft results from 59°N to 80°N latitude, *Geophys. Res. Lett.*, 17, 505, 1990.
- Toohey, D. W., J. G. Anderson, W. H. Brune, and K. R. Chan, In situ measurements of BrO in the Arctic stratosphere, *Geophys. Res. Lett.*, 17, 513, 1990.
- Mather, J. H., and W. H. Brune, Heterogeneous chemistry on liquid sulfate aerosols: A comparison of in situ measurements with zero-dimensional model calculations, *Geophys. Res. Lett.*, 17, 1283, 1990.
- Toohey, D. W., W. H. Brune, K. R. Chan, and J. G. Anderson, In situ measurements of midlatitude ClO in winter, *Geophys. Res. Lett.*, 18, 21, 1991.
- Brune, W. H., J. G. Anderson, D. W. Toohey, D. W. Fahey, S. R. Kawa, R. L. Jones, D. S. McKenna, and L. R. Poole, The potential for ozone depletion in the Arctic polar stratosphere, *Science*, 252, 1260, 1991.

- A. Radiative Flux Measurements
- B. PI Francisco P.J. Valero, Co-I Peter Pilewskie at NASA Ames Research Center, Moffett Field, CA 94035
- C. Research Objectives: To determine brightness temperatures in the boundary layer with the objective to model the radiative processes associated with polar stratospheric clouds and ozone depletion.
- D. Summary of Progress and Results: This project was funded in March 1991. A two channel infrared radiometer for use in the NASA DC-8 aircraft has been designed and is being built. Aircraft integration is in progress.
- E. Publications: None yet as this is a new project.

USE OF RADON AND COSMOGENIC RADIONUCLIDES IN THE STUDY OF  
STRATOSPHERE-TROPOSPHERE EXCHANGE PROCESSES

Dr. Mark A. Kritz, Principal Investigator

Atmospheric Sciences Research Center  
State University of New York  
Albany, NY 12222

RESEARCH OBJECTIVES:

To develop and apply means of using radon (Rn-222) and cosmogenic radionuclide (Be-7 and P-32) measurements to identify and quantify the exchange of air between troposphere and stratosphere.

SUMMARY OF PROGRESS AND RESULTS:

1) The Spring 1984 and Spring 1986 flight series of NASA's Stratosphere-Troposphere Exchange Project (STEP) studied intra-stratospheric transports and troposphere-to-stratosphere exchanges associated with cyclogenesis and tropopause folding in the vicinity of mid-latitude tropospheric jets.

Correlations of Be-7, ozone, water vapor and potential vorticity measured in the high shear regions above the jet core in the 1984 experiment were indicative of mixing between the cyclonic and anticyclonic sides of the jet and are consistent with the hypothesis that small-scale entrainments of upper tropospheric air into the lower stratosphere during cyclogenesis are important in maintaining the vertical gradients of Be-7, ozone, water vapor and other trace species in the lower few kilometers of the mid-latitude stratosphere. Correlations between Be-7 and ozone suggest a lower tropical stratosphere origin for the ozone-poor lamina observed above the jet core. These results are presented in Publication 1.

2) The goals of the 1987 STEP Tropical Experiment, conducted from Darwin, Australia, were to investigate the mechanisms and rates of irreversible transfer of mass, trace gases and aerosols from troposphere to stratosphere and within the lower tropical stratosphere, and to explain the observed dryness of the stratosphere. Radon, because of its unique origin in the lower troposphere and short (3.8 day) radioactive half life, was ideally suited as tracer for recent troposphere-to-stratosphere exchange, particularly because an analysis of the stratospheric Pb-210 budget (Publication 2) suggested that high radon concentrations ought to be present in tropospheric air entering the stratosphere.

A compact automatic radon measurement instrument was developed for and successfully flown in the STEP Tropical Experiment. Radon concentrations measured in regions of rapid vertical transport to the vicinity of the tropical tropopause were consistent with those predicted in Publication 2. A paper (Publication 3) presenting some of these results is in preparation and will be submitted in the fall of 1991.

3) During the development of the detectors for the STEP radon instrument a series of midlatitude upper tropospheric radon measurements were made piggy-backing on another NASA aircraft. These measurements revealed the systematic occurrence of unexpectedly high radon concentrations over the eastern Pacific. Trajectory and synoptic analyses showed this air originated in the Asian boundary layer, ascended in cumulus updrafts, and was carried eastward in the

mid-latitude jet, and suggest this process is an efficient mode of rapid long-range transport for other, chemically reactive atmospheric trace constituents of boundary layer origin. These results are presented in Publication 4.

#### PUBLICATIONS:

1. Kritz, M. A., S. W. Rosner, E. F. Danielsen and H. B. Selkirk, Air mass origins and troposphere-to-stratosphere exchange associated with mid-latitude cyclogenesis and tropopause folding inferred from Be-7 measurements, in press, Journal of Geophysical Research, 1991.
2. Lambert, G., J. C. LeRoulley and M. A. Kritz, Box model for radon transfers to the stratosphere, Tellus 42B, 135-141, 1990.
3. Kritz, M. A., S. W. Rosner and L. Pfister, Use of airborne radon measurements to follow rapid convective ascents in the STEP Tropical Experiment, in preparation.
4. Kritz, M. A., J. C. LeRoulley and E. F. Danielsen, The China Clipper---fast advective transport of radon-rich air from the Asian boundary layer to the upper troposphere near California, Tellus 42B, 46-61, 1990.



## Cloud Particle Measurements during AASE

James E. Dye, Darrel Baumgardner, and Bruce W. Gandrud  
National Center for Atmospheric Research

Guy V. Ferry  
NASA/Ames Research Center

### ABSTRACT OF RESEARCH OBJECTIVES

The Forward Scattering Spectrometer Probe (FSSP) Model 300 was developed for the Airborne Arctic Stratospheric Experiment (AASE) to make in-situ measurements of polar stratospheric cloud (PSC) and background sulfate particles in the size range of 0.4 to 20  $\mu\text{m}$  from the NASA ER-2 aircraft. The goals of this research were to evaluate, calibrate, characterize the limitations and assure reliable operation of the FSSP 300 for the AASE; to provide measurements of the number concentration, size and mass of particles in PSCs; and to increase our understanding of the physical and chemical mechanisms important in the formation of PSCs and the role of PSCs in the chemistry of the polar stratosphere.

### SUMMARY OF RESULTS

Evaluation of the FSSP 300 Operating Characteristics An intensive evaluation of the probe's operating characteristics has been made and its limitations determined. Measurements from this probe are affected by Mie scattering ambiguities, uncertainties in the index of refraction and shape of particles being measured, non-uniform laser illumination, uncertainties in the sample volume and electronic response time roll-off. Detailed examination of the uncertainties suggest a possible error in concentration measurements of about  $\pm 22\%$ , in overall sizing by about  $\pm 20\%$ , and therefore in mass, a combined error of about  $\pm 50\%$ .

Number and Size Characteristics of PSC Particles The analysis of measurements from the FSSP 300 during the AASE shows that in the Arctic most of the mass of the type I PSCs (presumed to be nitric acid trihydrate) is predominantly near 1  $\mu\text{m}$  diameter with total volumes of 0.5 to 5  $\mu\text{m}^3 \text{ cm}^{-3}$ . Particle concentrations of the type I PSC particles were from 2 to 15  $\text{cm}^{-3}$  with surface areas of 1 to 20  $\mu\text{m}^2 \text{ cm}^{-3}$ . The larger type II particles were encountered much less frequently and predominantly near the bottom of PSC clouds in locations in which the particles probably fell from higher altitudes, thus the FSSP 300 measurements represent lower limits. In these regions type II particle concentrations were from 0.001 to 0.01  $\text{cm}^{-3}$  with sizes up to 24  $\mu\text{m}$ , the upper size limit of the FSSP 300. Surface areas were 0.1 to 3  $\mu\text{m}^2 \text{ cm}^{-3}$  and volumes of 0.1 to 8  $\mu\text{m}^3 \text{ cm}^{-3}$ .

Physics of PSC particle formation The particle size distribution measurements in conjunction with measurements of temperature, water vapor,  $\text{N}_2\text{O}$ , and  $\text{NO}_y$  made by other investigators show that in the Arctic the majority of the type I PSCs do not occur until temperatures of 192 K and apparent supersaturations of nitric acid with respect to nitric

acid trihydrate of almost 10 are reached, whereas in the Antarctic type I PSC formation occurred near saturation ratios near 1. In the Arctic, large regions exist in which type I particle formation is thermodynamically stable but particles do not occur. The combined measurements provide additional support to the hypothesis that type I PSC particles have a nitric acid trihydrate composition.

Examination of the changes in particle volume with decreasing temperature for the background sulfate aerosol suggests that near the Arctic polar region (and therefore also in the low and mid latitude stratosphere) most of the stratospheric sulfuric acid particles remain liquid until temperatures in an air mass decrease to at least 192 K. The evidence suggests that in the Arctic the freezing of supercooled sulfuric acid droplets may play a precursor role in the formation of PSC particles.

#### JOURNAL PUBLICATIONS

- Dye, J. E., B. W. Gandrud, D. Baumgardner, L. Sanford, and G. V. Ferry, 1990: A survey of particle measurements in the Arctic from the Forward Scattering Spectrometer Probe model 300. *Geophys. Res. Lett.*, 17, 409–412.
- Dye, J. E., B. W. Gandrud, D. Baumgardner, K. R. Chan, G. V. Ferry, M. Loewenstein, K. K. Kelly, and J. C. Wilson, 1990: Observed particle evolution in the polar stratospheric cloud of January 24, 1989. *Geophys. Res. Lett.*, 17, 413–416.
- Gandrud, B. W., J. E. Dye, D. Baumgardner, G. V. Ferry, M. Loewenstein, K. R. Chan, L. Sanford, B. Gary, and K. K. Kelly, 1990: The January 30, 1989 Arctic Polar Stratospheric Cloud (PSC) event: Evidence for the mechanism of dehydration. *Geophys. Res. Lett.*, 17, 457–460.
- Poole, L. R., S. Solomon, B. W. Gandrud, K. A. Powell, J. E. Dye, R. L. Jones, and D. L. McKenna, 1990: The Polar Stratospheric Cloud event of January 24, 1989 Part 1. Microphysics. *Geophys. Res. Lett.*, 17, 537–540.
- Wofsy, S. C., R. J. Salawitch, J. H. Yettaw, M. B. McElroy, B. W. Gandrud, J. E. Dye, and D. Baumgardner, 1990: Condensation of HNO<sub>3</sub> on falling ice particles: Mechanism for dehydration of the polar stratosphere. *Geophys. Res. Lett.*, 17, 437–440.
- Dye, J. E., D. Baumgardner, B. W. Gandrud, S. R. Kawa, K. K. Kelly, M. Loewenstein, G. V. Ferry, K. R. Chan, B. L. Gary, 1991: Particle size distribution in Arctic polar stratospheric clouds growth and nucleation of sulfuric acid droplets and implications for cloud formation, accepted *J. Geophys. Res.*
- Baumgardner, D., J. E. Dye, R. G. Knollenberg, and B. W. Gandrud, 1991: Interpretation of measurements made by the FSSP-300 during the airborne Arctic stratospheric expedition, accepted *J. Geophys. Res.*
- Kawa, S. R., D. W. Fahey, K. K. Kelly, J. E. Dye, D. Baumgardner, B. W. Gandrud, M. Loewenstein, G. V. Ferry, K. R. Chan, 1991: The Arctic polar stratospheric cloud aerosol: aircraft measurements of reactive nitrogen, total water, and particles, accepted *J. Geophys. Res.*

**A. Title of Research Task:**

Particle Chemistry Impactor Experiment

**B. Investigators and Institutions:**

Rudolf F. Pueschel, MS 245-4, NASA Ames Research Center, Moffett Field, CA 94035-1000

Kenneth G. Snetsinger, MS 245-4, NASA Ames Research Center, Moffett Field, CA 94035-1000.

Guy V. Ferry, MS 245-4, NASA Ames Research Center, Moffett Field, CA 94035-1000

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John Hallett, Desert Research Institute, University of Nevada, Reno, NV 89506-0220

**C. Abstract of Research Objectives:**

Polar stratospheric cloud particles are collected on impactors and investigated with regard to physical (size, shape, phase), chemical (elemental and chemical composition), and optical properties to help understand their formation and their role in stratospheric ozone depletion.

**D. Summary of Progress and Results**

The nitric, hydrochloric and sulfuric acid content of stratospheric aerosol particles collected during the Arctic Airborne Stratospheric Experiment (AASE) in January/February 1989 was determined. Nitric acid was found to condense at  $194.4 \pm 4.0$  K. This temperature is similar to the threshold temperature of nitric acid condensation in the Antarctic stratosphere, and at which an increase in light extinction is seen by the SAMII satellite sunphotometer. Thus, nitric acid appears to be a compound that is commonly found in Arctic and Antarctic polar stratospheric clouds.

A comparison of particle counts by an optical spectrometer with those from the wire impactors during AASE contributed to an understanding of a heterogeneous nucleation mechanism of type I polar stratospheric cloud formation: The Arctic stratospheric aerosol consists of a few per cubic centimeter of dilute sulfuric acid droplets. As the temperature is lowered, more water is taken up by the particles. Some of the particles become dilute enough to (>50% weight percent H<sub>2</sub>O) to take on hydrochloric acid. When the temperature gets as cold as 195K, nitric acid condenses on the particles, causing an average increase in size by about a factor of three, and an increase in volume by a factor of about 30. Computation of the light extinction property of this aerosol confirms the seasonal increase in optical depths that are regularly seen by the SAMII satellite sunphotometer.

#### **E. Journal Publications:**

R.F.Pueschel, K.G.Snetsinger, J.K.Goodman, O.B.Toon, G.V.Ferry, V.R.Oberbeck, J.M.Livingston, S.Verma, W.Fong, W.L.Starr, and K.R.Chan, Condensed Nitrate, Sulfate and Chloride in Antarctic Stratospheric Aerosols, *J.Geophys.Res.*, **94**, 11271-11284, 1989.

R.F.Pueschel, K.G.Snetsinger, P.Hamill, J.Goodman, and M.P.McCormick, Nitric acid in Polar Stratospheric Clouds: Similar Temperature of Nitric Acid Condensation and Cloud Formation, *Geophys.Res.Lett.*, **17**, 429-432, 1990.

R.F.Pueschel (Ed.), Proceedings of an International Workshop: Stratospheric Aerosols-Measurements, Properties and Effects, NASA Conf.Pub. 3114, 1991.

R.F.Pueschel, G.V.Ferry, K.G.Snetsinger, J.Goodman, J.E.Dye, D.Baumgardner, and B.Gandrud, An Example of Type I Polar Stratospheric Cloud Formation by Hetrogeneous Nucleation, *J.Geophys.Res.*, accepted for publication.

## RESEARCH SUMMARY 1990-1991

### COUNTING CONDENSATION NUCLEI IN THE ANTARCTIC OZONE MISSION RESEARCH GRANT NAG 2-458

- B. James Charles Wilson, Principal Investigator  
University of Denver
- C. The main research objective for 1990-1991 was to improve our characterization of the stratospheric sulfate aerosol both in and out of the polar vortex. This involved several tasks:
1. Analyze the performance of the inlet of the Passive Cavity Aerosol Spectrometer (PCAS) for the effects of aerosol evaporation and anisokinetic sampling. Submit data corrected for these effects to the Airborne Arctic Stratospheric Expedition (AASE) data archive.
  2. Analyze data taken with the ER-2 Condensation Nucleus Counter (ER2-CNC) and the Passive Cavity Aerosol Spectrometer (PCAS) in AASE and submit papers for publication.
  3. Study the performance of the sampling inlet of the PCAS in order to improve our ability to obtain accurate samples from the ER-2. Topics studied included the actual wind vector at the sampling location and the air flow in diffusers having large area ratios.
  4. Cooperate with NASA Ames and Particle Measuring Systems Inc. in the upgrade of the PCAS to a Focused Cavity Aerosol Spectrometer (FCAS) which measures particles as small as  $0.05\mu\text{m}$  in diameter. Calibrate the FCAS in the Airborne Arctic Stratospheric Experiment II.
  5. Operate the ER-2 CNC in the Airborne Arctic Stratospheric Experiment II.
- D. Progress and Results
1. The AASE data were analyzed. Measured size distributions of sulfate aerosol were corrected for the effects of anisokinetic sampling and particle evaporation and were reported for inclusion in the AASE Data Archive (Edition 2, 1990).
  2. New particle production was observed in the northern hemisphere polar vortex in AASE and was reported.
  3. Sulfate size distributions measured in AASE with the ER-2 CNC and the PCAS were reported. A nucleation mode, with mean diameter between  $0.01\mu\text{m}$  and  $0.1\mu\text{m}$ , was found to occur in the polar vortex where new particle formation was observed. A nucleation mode was also found to occur in the bottom few kilometers of the stratosphere. This mode probably occurs at all latitudes.
  3. The wind vector was measured at the location of the PCAS inlet. The results will permit the orientation of the inlet to be corrected for the effects of the aircraft on the airflow.
  4. The Focused Cavity Aerosol Spectrometer was characterized and calibrated for AASE II.

## E. Publications

Wilson, J.C., M. R. Stolzenburg, W. E. Clark, M. Loewenstein, G. V. Ferry, K. R. Chan, "Measurements of Condensation Nuclei in the Airborne Arctic Stratospheric Expedition: Observations of Particle Production in the Polar Vortex", *Geophysical Res. Lett.*, 17:361-364, 1990.

Pueschel, R. F., V. R. Oberbeck, K.G. Snetsinger, P.B. Russell, J. C. Wilson, J. M. Livingston, G. V. Ferry, S. Verma, W. Fong, "Calibration correction of an active scattering spectrometer probe to account for refractive index of stratospheric aerosols: comparison of results with inertial impaction", *Journal of Aerosol Science and Technology*, 12: 992-1002, 1990.

Dye, J. E., B. W. Gandrud, D. Baumgardner, K.R. Chan, G. V. Ferry, M. Loewenstein, K.K. Kelly, J.C. Wilson, "Observed particle evolution in the polar stratospheric cloud of January 24, 1989", *Geophysical Res. Lett.*, 17: 413-416, 1990.

Wilson, J. C., M. R. Stolzenberg, W. E. Clark, M. Loewenstein, G. V. Ferry, K. R. Chan, R. Kawa, K. K. Kelly, "Stratospheric sulfate aerosol in and near the northern hemisphere polar vortex: The morphology of the sulfate layer, multimodal size distributions and the effect of denitrification", accepted pending minor revisions, *Journal of Geophysical Research*, 1991.

# AIRBORNE MICROWAVE TEMPERATURE PROFILER INVESTIGATIONS OF ATMOSPHERIC DYNAMICS RELATED TO OZONE DEPLETION

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Jet Propulsion Laboratory  
Pasadena, CA 91109

## Research Objectives

A Microwave Temperature Profiler instrument, MTP, is mounted in NASA's ER-2 research aircraft. MTP measures profiles of air temperature versus altitude for a region 2 km below to 3 km above the ER-2 aircraft. This is accomplished using passive radiometric remote sensing techniques. Temperature profiles generated by the MTP instrument have been used during airborne campaigns in the Arctic and the Antarctic to study stratospheric ozone depletion. The MTP data have been used to support scientific investigations of processes that remove water vapor and nitric acid from the lower stratosphere in the winter-time polar vortex. "Denitrification" of the polar vortex is one crucial precondition for stratospheric ozone depletion.

Several observational objectives contribute to the above scientific objective. The MTP instrument has been used for: 1) the measurement and statistical characterization of vertical motions of air parcels for timescales of tens of minutes, which are needed for properly constraining model representations of microphysical processes that influence the formation and "evaporation" of Polar Stratosphere Clouds, PSCs, 2) the detection and characterization of "mountain waves" in the lower stratospheric polar vortex, 3) the location of altitude regimes above the ER-2 where the air is cold enough to produce PSCs, and 4) locating the polar vortex boundary by enabling a more accurate determination of potential vorticity versus latitude along flight paths into and out of the polar vortex.

## Progress and Results

MTP profiles of air temperature are used to produce "altitude/ground track" cross-sections of the altitudes of potential temperature surfaces. For cross-sections oriented parallel to the wind, potential temperature surfaces can be viewed as equivalent to streamlines, thus enabling inferences to be made about vertical displacements of air parcels. Such analyses have shown that air parcels in the lower stratosphere have an ever-present component of "up and down" motion that would not be predicted to exist using synoptic-scale weather data. These mesoscale vertical motions produce large cooling and warming rates, with magnitudes of several hundred degrees per day and fluctuation timescales of tens of minutes. It has been conjectured that such large heating and cooling cycles, superimposed as they are upon the more commonly modeled small-amplitude synoptic scale heating and cooling, may profoundly alter particle size distributions of PSCs, and thus affect the subsequent falling out of large particles which carry nitric acid to lower altitudes.

Occasionally, large aerosol particles are encountered by *in situ* instruments at times when the ambient air temperature is too warm for either water vapor or nitric acid vapor to condense. On many of these occasions MTP temperature profiles reveal that air temperatures are sufficiently cold for PSC formation only 1 or 2 km above ER-2 flight level. Thus, according to recent suggestions, the *in situ* particles are probably "snow" falling from PSCs located above the ER-2. For particles to fall 1 or 2 km without completely evaporating requires special conditions, with interesting implications for the denitrification process.

## Publications

Bacmeister, J. T., *et al*, "Small-Scale Waves Encountered During AASE," *Geophys. Res. Lett.*, 17, p 349-352, March 1990.

Gandrud, B. W., *et al*, "The January 30, 1989 Arctic Polar Stratospheric Clouds (PSC) Event: Evidence for a Mechanism of Dehydration," *Geophys. Res. Lett.*, 17, p 457-460, March 1990.

Dye, J. E., *et al*, "Particle Size Distributions in Arctic Polar Stratospheric Clouds: Growth and Nucleation of Sulfuric Acid Droplets and Implications for Cloud Formation," *J. Geophys. Res.*, *in press*.

## SUMMARY OF UPPER ATMOSPHERIC RESEARCH

A. Title of Research Task: Whole Air Sampler

B. Investigators and Institutions:  
James F. Vedder, San Jose State University Foundation  
NASA Ames Research Center

C. Abstract of Research Objectives: Minor constituents play an important role in upper atmospheric photochemistry and serve as tracers in transport and mixing studies in tropospheric-stratospheric exchange processes. Measurements of trace gases are essential to an understanding of the mechanisms by which minor constituents originating in the troposphere, both naturally occurring and anthropogenic, reach the stratosphere; data on tracer distributions thus acquired are important in the development of models for predicting photochemical effects in the stratosphere.

D. Summary of Progress and Results: The work reported here is a joint effort of NASA Ames Research Center and the National Center for Atmospheric Research. NCAR is funded separately by NASA Headquarters.

Since the participation in the Airborne Arctic Stratospheric Expedition in 1989, the Whole-Air Sampler for the ER-2 has been modified to carry up to 29 sampling canisters. The original instrument carried 14 canisters. In addition, the original electronic controller for the system has been replaced by a more versatile unit. In May, 1991, the electrical and mechanical integration of the modified Whole-Air Sampler was completed; but the scheduled test flight was cancelled because of poor weather. In August, 1991, the test flights were accomplished for the Whole-Air Sampler along with the other instruments to be used in the Airborne Arctic Stratospheric Expedition II.

Utilization of the data collected during the Airborne Antarctic Ozone Experiment and the Airborne Arctic Stratospheric Expedition continued during the period covered by this report. Some analyses of the measurements were presented at the Fall Meeting of the American Geophysical Union in 1989, and several journal articles have been published.

E. Journal Publications

Redistribution of Reactive Odd Nitrogen in the Lower Arctic Stratosphere (1990): G. Hubler, D. W. Fahey, K. K. Kelly, D. D. Montzka, M. A. Carroll, A. F. Tuck, L. E. Heidt, W. H. Pollock, G. L. Gregory, and J. F. Vedder, Geophysical Research Letters, **17**, 453-456.

A Comparison of ER-2 Measurements of Stratospheric Water Vapor Between the 1987 Antarctic and 1989 Arctic Airborne Missions. K. K. Kelley, A. F. Tuck, L. E. Heidt, M. Loewenstein, J. R. Podolske, S. R. Strahan, and J. F. Vedder. Geophysical Research Letters, **17**, 465-468.



## NASA Research Summary

### A. Trace-Gas Measurements from Whole-Air Sampling

B. L.E. Heidt and G.P. Brasseur

C. The objectives of this research in 1990 and 1991 were:

- (1) To continue analysis and publication of the data collected during the Airborne Arctic Stratospheric Expedition (AASE),
- (2) modify WAS to increase number of samples collected from 14 to 29,
- (3) conduct intercomparison of measurements of  $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  with R. Weiss of Scripps Institution of Oceanography,
- (4) conduct intercomparisons of calibration standards with other laboratories to include as many trace gases of interest as possible, and
- (5) develop and calibrate analytical techniques to measure CFC replacements, primarily  $\text{CHClF}_2$ ,  $\text{C}_2\text{Cl}_2\text{F}_4$ ,  $\text{C}_2\text{ClF}_5$ ,  $\text{C}_2\text{HClF}_2$ , and  $\text{C}_2\text{H}_2\text{F}_4$ .

D. Interpretation of AASE-I data has been and continues to be in collaboration with Guy Brasseur (NCAR/Atmospheric Chemistry Division Director), Susan Solomon (NOAA/Aeronomy Laboratory), and other principal investigators of the expedition. These collaborations have resulted in new determinations of lifetimes based on measurements, studies of the relative roles of chemistry and transport, and studies of partitioning in the  $\text{Cl}_x$  and  $\text{NO}_x$  families.

Modifications to the WAS have been completed and certified. The new payload operated successfully in recent test flights from Moffett Field.

The blind intercomparison of AASE-I samples has been successfully completed (see examples attached). The intercalibration of standards is scheduled to begin the first week of September.

The development and calibration of analytical techniques to measure the CFC replacements has been completed. This work, which has a major impact on both the lifetimes and photochemistry cycles of the HCFC's, included measurements of the remaining samples from AASE-I. This collaborative effort (with S. Solomon) has been submitted to the *Journal of Geophysical Research*.

## NASA Research Summary

### E. Publications resulting from contract support in 1990 and 1991.

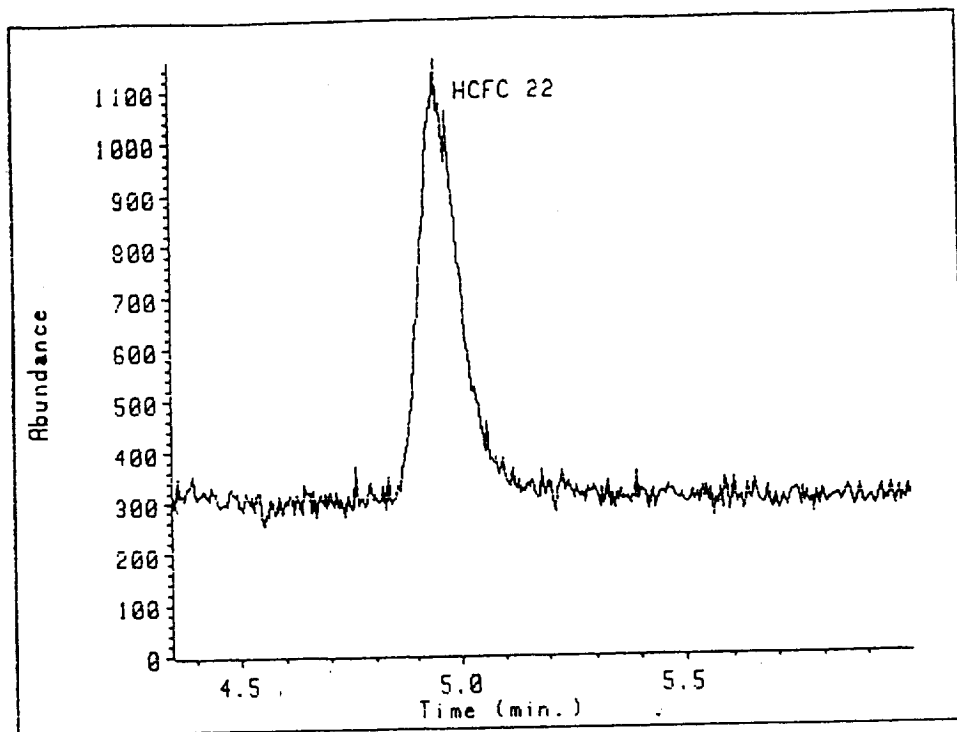
Observations of denitrification and dehydration in the winter polar stratosphere; D.W. Fahey, K.K. Kelly, S.R. Kawa, A.F. Tuck, M. Lowenstein, K.R. Chan, and L.E. Heidt, *Nature*, Vol. 344, no. 6264, pg. 321-324, March, 1990.

Redistribution of reactive odd nitrogen in the lower Arctic stratosphere; G. Hübler, D.W. Fahey, K.K. Kelly, D.D. Montzka, M.A. Carroll, A.F. Tuck, L.E. Heidt, W.H. Pollock, J.F. Vedder, and G.L. Gregory, to *J. Geophys. Res.*

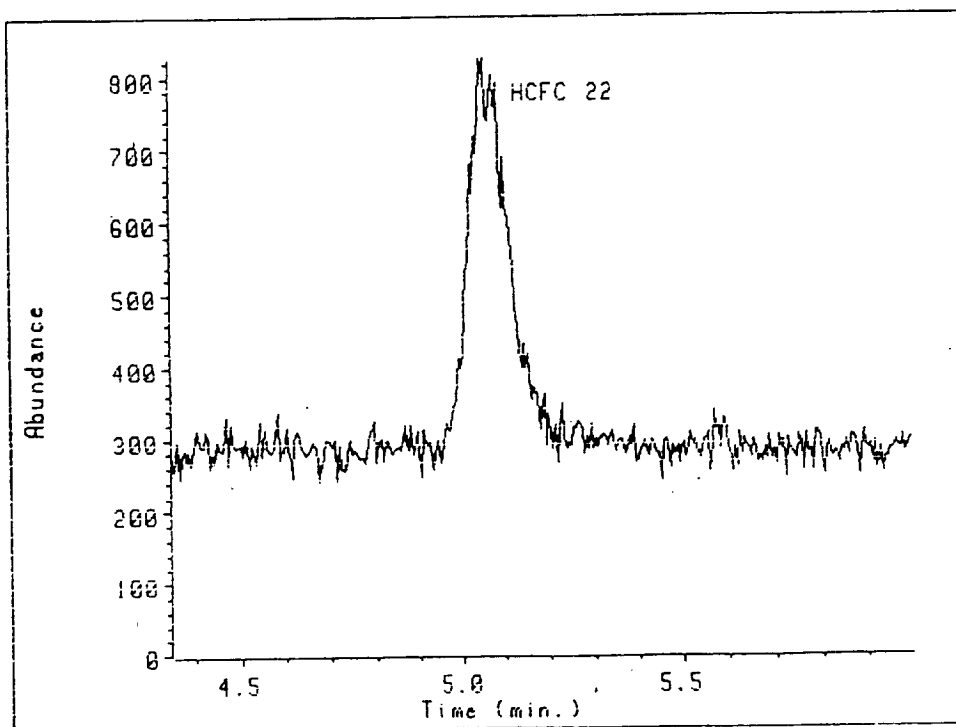
Photochemical partitioning of the reactive nitrogen and chlorine reservoirs in the high-latitude stratosphere; S.R. Kawa, D.W. Fahey, S. Solomon, M.H. Proffitt, L.E. Heidt, W.H. Pollock, W.H. Brune, D.W. Toohey, J.G. Anderson, D.E. Anderson, and M. Lowenstein, to *J. Geophys. Res.*

On the evaluation of ozone depletion potentials; S. Solomon, M. Mills, L.E. Heidt, W.H. Pollock, and A.F. Tuck, to *J. Geophys. Res.*

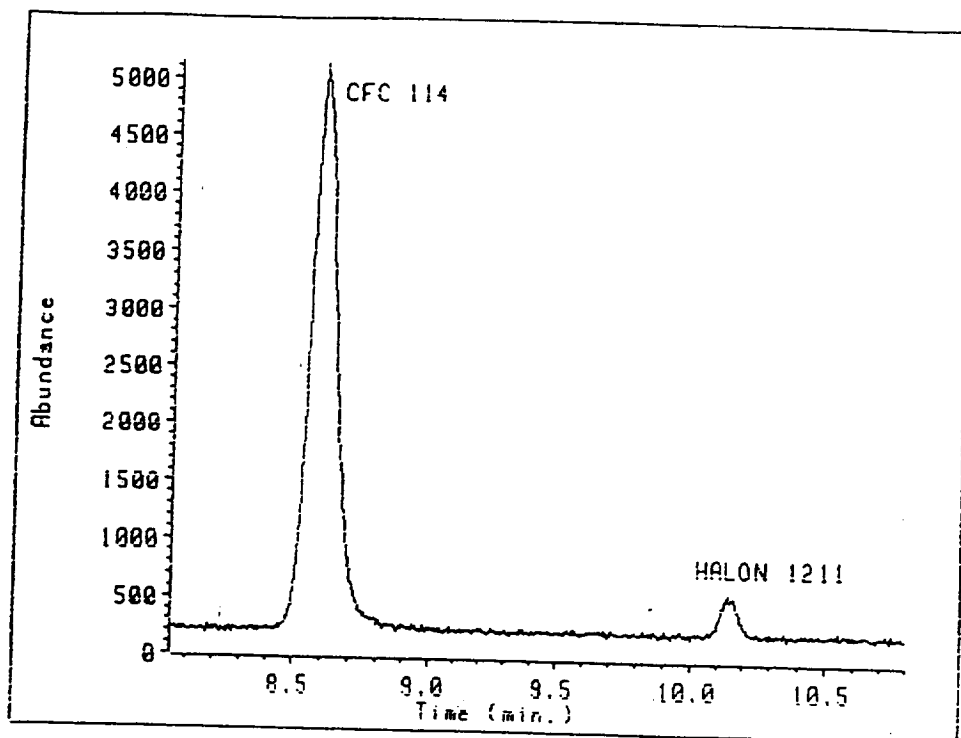
Aging of the Arctic polar vortex air; S.J. Hovde, L.E. Heidt, A.F. Tuck, to *J. Geophys. Res.*



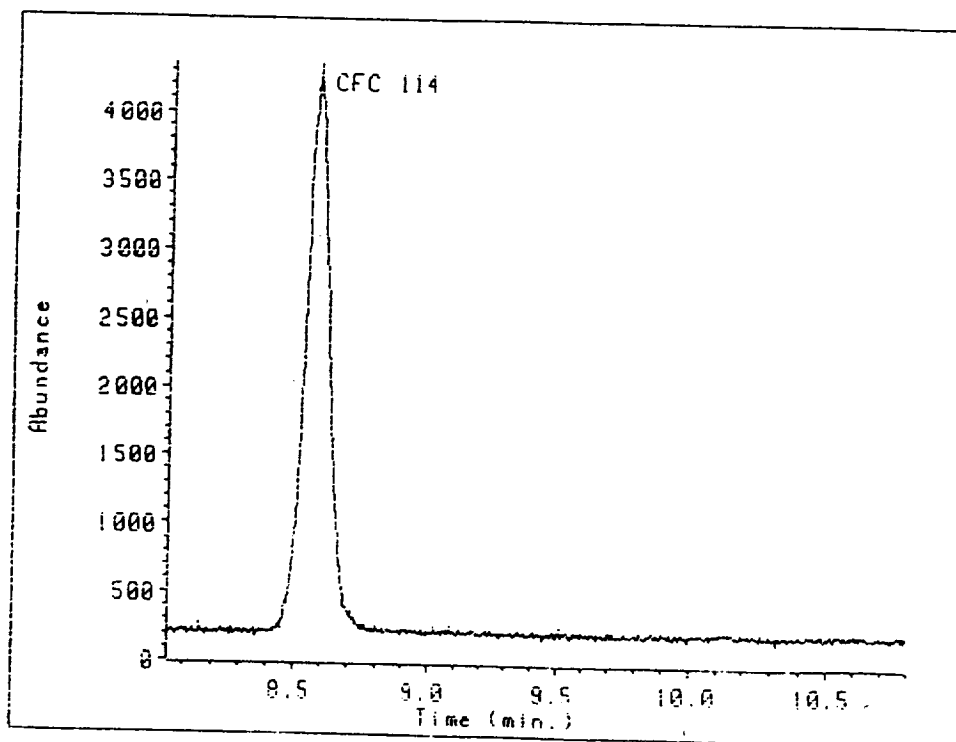
ER-2 FLIGHT 1-12-89  
ALTITUDE 19.9 Km  
OUTSIDE VORTEX  
SAMPLE VOLUME 202 ml



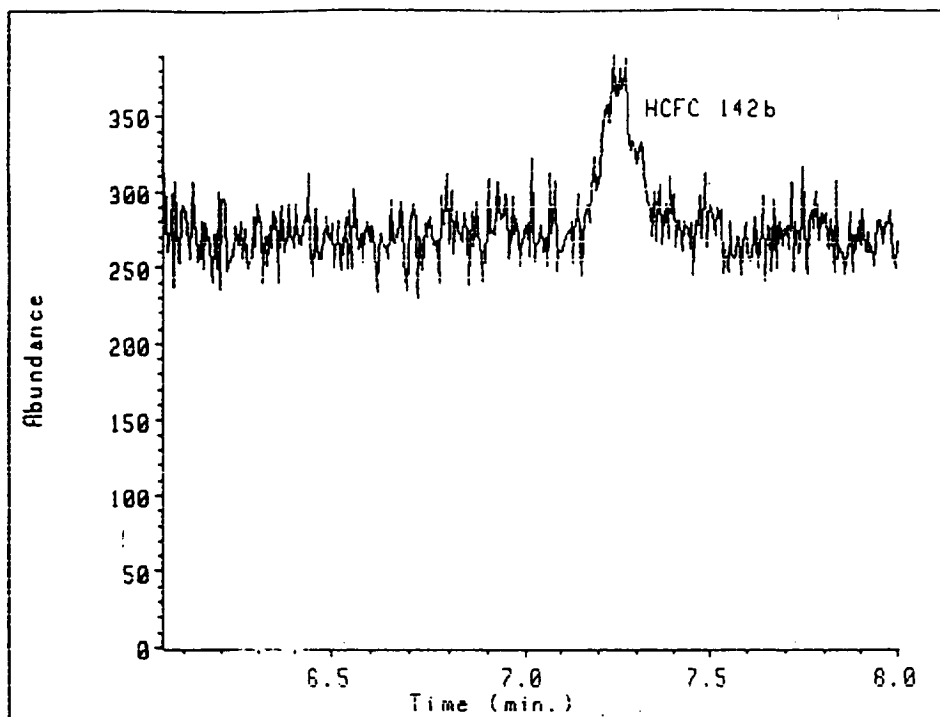
ER-2 FLIGHT 1-12-89  
ALTITUDE 20.3 Km  
INSIDE VORTEX  
SAMPLE VOLUME 202 ml



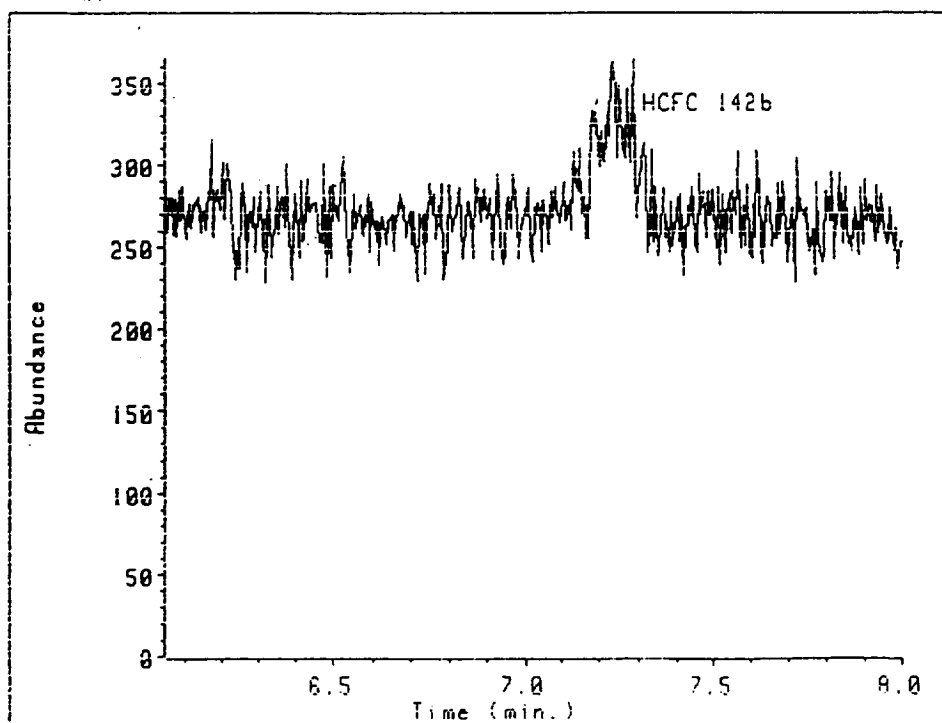
ER-2 FLIGHT 1-12-89  
ALTITUDE 19.9 Km  
OUTSIDE VORTEX  
SAMPLE VOLUME 1414 ml



ER-2 FLIGHT 1-12-89  
ALTITUDE 20.3 Km  
INSIDE VORTEX  
SAMPLE VOLUME 1596 ml



ER-2 FLIGHT 1-12-89  
ALTITUDE 19.9 Km  
OUTSIDE VORTEX  
SAMPLE VOLUME 1414 ml



ER-2 FLIGHT 1-12-89  
ALTITUDE 20.3 Km  
INSIDE VORTEX  
SAMPLE VOLUME 1596 ml

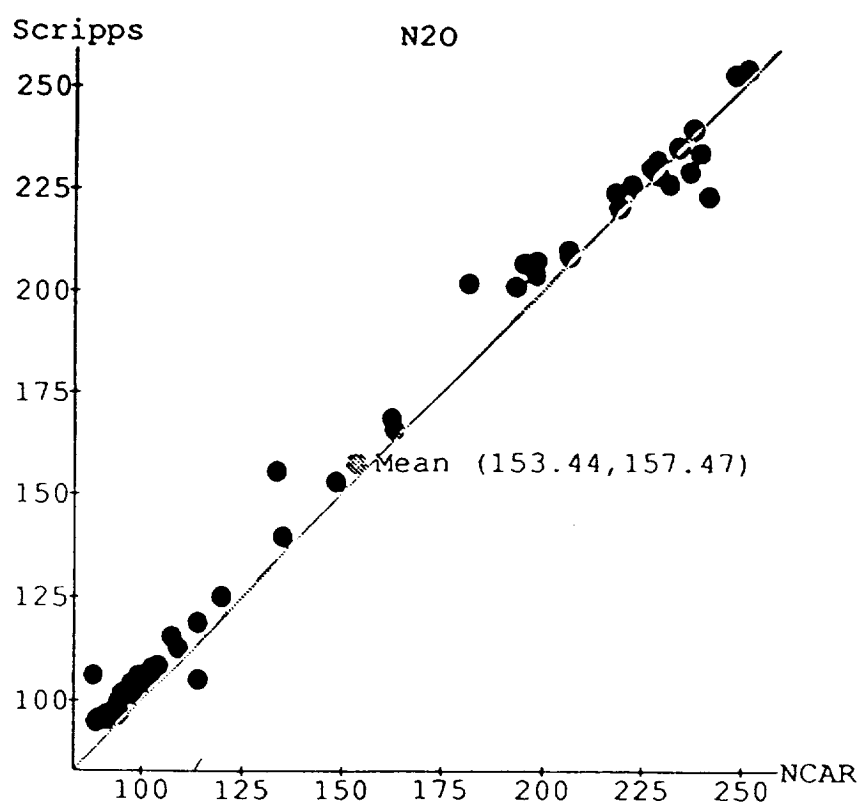


FIGURE 5

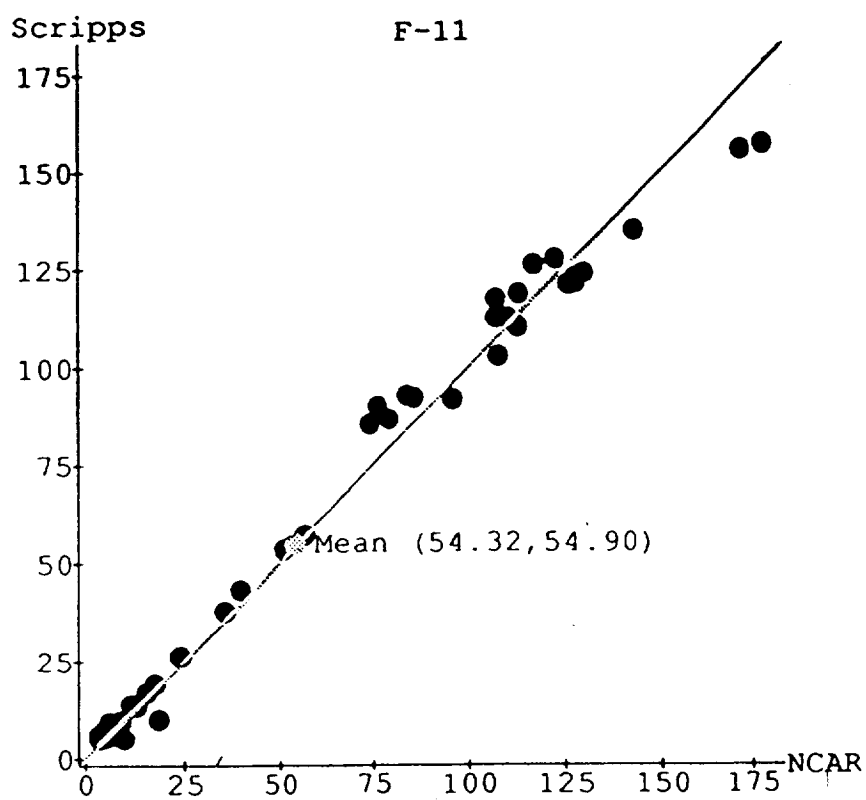


FIGURE 6

## NASA Research Summary

### A. Measurements of Chemical Constituents in the Arctic Stratosphere

B. M.T. Coffey and William G. Mankin  
National Center for Atmospheric Research  
P.O. Box 3000  
Boulder, Colorado 80307

C. Objectives of this research in 1990 and 1991 were to continue analysis of the data collected during the Airborne Arctic Stratospheric Expedition (AASE), participate in the design and planning for the Network for the Detection of Stratospheric Change, prepare for the second airborne Arctic field campaign and respond to other stratospheric measurement opportunities.

D. Analysis of the observations from the AASE and the Airborne Antarctic Observation Experiment is still underway and has resulted in a number of publications, as listed below. We continue to prepare for installation, in October 1991, of our infrared spectrometer onboard the NASA DC-8 aircraft for flights in the Arctic between November 1991 and March 1992.

Another aspect of our NASA sponsored activities was participation (by W.G. Mankin) in the steering committee of the Network for the Detection of Stratospheric Change. The steering committee met twice during this period to refine plans for deployment of the network. Mankin chaired the site selection working group which gathered information on potential sites and prepared a report which was the basis of the site selection. He also chaired the infrared working group which met to define common infrared instrument parameters and to plan for developing standard data reduction methods.

In connection with our stratospheric observation program we took advantage of a rare opportunity to observe the cloud of gas and particles injected into the stratosphere by the Pinatubo volcano in June 1991. With only a week's notice we installed our Fourier transform spectrometer aboard the NASA Wallops Flight Facility Electra aircraft for a week long field program at low latitude. During that program we measured the amounts of a number of gases in the plume. Results for SO<sub>2</sub>, HCl and O<sub>3</sub> are reported in a paper submitted to *Geophysical Research Letters*.



#### E. Publication resulting from NASA sponsorship

Airborne measurements of stratospheric constituents over the Arctic in the winter of 1989, W. G. Mankin, M. T. Coffey, A. Goldman, M. R. Schoeberl, L. R. Lait, P. A. Newman, *Geophys. Res. Lett.*, **17**, 473-476, 1990.

Three dimensional simulations of hydrogen chloride and hydrogen fluoride during the airborne arctic stratosphere expedition, J. A. Kaye, A. R. Douglass, R. B. Rood, R. S. Stolarski, P. A. Newman, D. J. Allen, E. M. Larson, M. T. Coffey, W. G. Mankin, G. C. Toon, *Geophys. Res. Lett.*, **17**, 529-532, 1990.

Heterogeneous conversion of COF<sub>2</sub> to HF in polar stratospheric clouds, S. C. Wofsy, J. H. Yatteau, R. J. Salawitch, M. B. McElroy, G. C. Toon, W. G. Mankin, and M. T. Coffey, *Geophys. Res. Lett.*, **17**, 461-464, 1990.

Effects of atmospheric motions on nitrogen and chlorine compounds in the Arctic stratosphere, J. H. Yatteau, S. C. Wofsy, R. J. Salawitch, M. B. McElroy, M. R. Schoeberl, L. R. Lait, P. A. Newman, A. Torres, W. G. Mankin, M. T. Coffey, G. C. Toon, M. Lowenstein, J. Podolske, S. E. Strahan, K. R. Chan, and M. H. Proffitt, *Geophys. Res. Lett.*, **17**, 533-536, 1990.

Studies of arctic stratospheric ozone in a 2-D model including some effects of zonal asymmetries, I. S. A. Isaksen, B. Rognerud, F. Stordal, M. T. Coffey, and W. G. Mankin, *Geophys. Res. Lett.*, **17**, 473-476, 1990.

Airborne Observations of SO<sub>2</sub>, HCl and O<sub>3</sub> in the Stratospheric Plume of the Pinatubo Volcano in July 1991, M.T. Coffey, A. Goldman and W.G. Mankin, submitted to *Geophys. Res. Lett.*, 1991.

# AIRBORNE LIDAR STRATOSPHERIC OZONE AND AEROSOL INVESTIGATIONS

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Hampton, VA 23665-5225

## Research Objectives:

The objectives of this research are to investigate the distribution of ozone ( $O_3$ ) and aerosols across the polar regions during the fall, winter, and spring periods and to relate these observations to chemical and dynamical processes that can contribute to the destruction of stratospheric  $O_3$ . The distribution and characteristics of stratospheric aerosols and polar stratospheric clouds (PSC's) are required to understand heterogeneous chemical processes that can lead to  $O_3$  depletion, and observations of  $O_3$  distributions are important in the direct detection of the spatial and temporal variations of  $O_3$  depletion. An airborne Differential Absorption Lidar (DIAL) system is operated in a zenith mode from the NASA DC-8 aircraft to obtain remote measurements of aerosols/PSC's and  $O_3$  in the lower stratosphere on long-range flights over the polar regions. The observed variability of  $O_3$  and aerosols is related to the atmospheric processes that contribute to the onset of  $O_3$  depletion and to the amount and distribution of the resulting  $O_3$  depletion.

## Progress and Results:

The analyses of the airborne lidar data from the Airborne Arctic Stratospheric Experiment (AASE-I) conducted in January-February 1989 were completed, and the results were published in a special issue of *Geophysical Research Letters* (see publication list below). Large-scale distributions of stratospheric  $O_3$  and aerosols were measured with the airborne lidar on 15 long-range flights into the polar vortex from Stavanger, Norway, during AASE-I. PSC's were observed in the polar vortex on 10 of 11 flights between January 6 and February 2, and the altitude range of most of the PSC's was from 14 to 27 km. On the early missions, two types of PSC's with distinctly different optical characteristics were observed for aerosols thought to be composed of nitric acid trihydrate. The first type observed (Type 1a) had low scattering ratios and large depolarization ratios, and the second type (Type 1b) had large scattering ratios and low depolarization ratios. It is thought that the Type 1a PSC's are responsible for the denitrification of the Arctic vortex and the Type 1b PSC's are more important in the heterogeneous processes that are related to  $O_3$  destruction. Water ice clouds (Type 2 PSC's) were also seen on a few occasions with very high scattering ratios and high depolarization ratios.

The observed O<sub>3</sub> distribution on the first flight into the polar vortex during AASE-I reflected the result of diabatic cooling of the air inside the vortex during the winter. On a potential temperature surface, the O<sub>3</sub> mixing ratio increased when going from outside to inside the vortex. The trend in the O<sub>3</sub> mixing ratio and potential vorticity distributions were found to be well correlated over the entire atmospheric cross section. On the last mission flown into the polar vortex on February 9, the O<sub>3</sub> in the potential temperature range from ~420 to 580 K was observed to be lower in the region between 71-80° N than farther inside the vortex. This was determined to be due to chemical O<sub>3</sub> depletion processes. A similar region was observed inside the vortex over Canada on the return flight from Norway to California on February 15.

All preparations for the 1991-92 AASE-II mission to investigate the chemical evolution of the Arctic polar vortex during the fall and winter periods have been completed. This field experiment will consist of a series of DC-8 flights across the Arctic polar vortex during 10-day missions conducted every month from November 1991 through March 1992. The airborne lidar system used during the AASE-I expedition has been modified for improved measurements of O<sub>3</sub>, aerosols, and PSC's during the AASE-II.

#### Journal Publications:

Browell, E. V., C. F. Butler, S. Ismail, P. A. Robinette, A. F. Carter, N. S. Higdon, O. B. Toon, M. R. Schoeberl, and A. F. Tuck, Airborne lidar observations in the wintertime Arctic stratosphere: Polar stratosphere clouds, *Geophys. Res. Lett.*, 17, 385-388, 1990.

Browell, E. V., C. F. Butler, S. Ismail, M. A. Fenn, S. A. Kooi, A. F. Carter, A. F. Tuck, O. B. Toon, M. H. Proffitt, M. Loewenstein, M. R. Schoeberl, I. Isaksen, and G. Braathen, Airborne lidar observations in the wintertime Arctic stratosphere: Ozone, *Geophys. Res. Lett.*, 17, 325-328, 1990.

Toon, O. B., E. V. Browell, S. Kinne, and J. Jordan, An analysis of lidar observations of polar stratospheric clouds, *Geophys. Res. Lett.*, 17, 393-396, 1990.

Lait, L. R., M. R. Schoeberl, P. A. Newman, M. H. Proffitt, M. Loewenstein, J. R. Podolske, S. E. Strahan, K. R. Chan, B. Gary, J. J. Margitan, E. V. Browell, M. P. McCormick, and A. Torres, Reconstruction of O<sub>3</sub> and N<sub>2</sub>O fields from ER-2, DC-8, and balloon observations, *Geophys. Res. Lett.*, 17, 521-524, 1990.

Browell, E. V., Differential Absorption Lidar Detection of Ozone in the troposphere and lower stratosphere, in *Optoelectronics for Environmental Science*, edited by S. Martellucci and A. N. Chester, pp. 77-89, Plenum Press, New York, 1990.

Grant, W. B., E. V. Browell, N. S. Higdon, and S. Ismail, Generation of 302-nm laser radiation for ozone DIAL measurements, *Appl. Opt.*, 30, 2628-2633, 1991.

A. TITLE OF RESEARCH TASK: Airborne Aerosol Lidar (RTOP 464-14-35-70)

B. INVESTIGATOR: Lamont R. Poole  
Atmospheric Sciences Division  
NASA Langley Research Center  
Hampton, VA 23665

C. ABSTRACT. The objectives of this research are: (1) to analyze dual-polarization and multi-wavelength airborne lidar measurements of aerosols and polar stratospheric clouds (PSCs) obtained during the Airborne Antarctic Ozone Experiment (AAOE) and the Airborne Arctic Stratospheric Expedition (AASE); and (2) to combine lidar, satellite, and other ancillary data with theoretical modeling calculations to investigate PSC characteristics.

D. SUMMARY OF PROGRESS AND RESULTS. AASE data obtained by the Langley dual-polarization aerosol lidar system ( $\lambda = 0.532 \mu\text{m}$ ) and the SAM II and SAGE II satellite sensors were used to study the microphysics and spatial characteristics of PSCs. Lidar observations of Type 1 PSCs were consistent with a nitric acid trihydrate particle composition and showed scattering ratios ranging up to 6 and, in general, very small depolarization ratios. Type 2 PSCs showed much larger scattering and depolarization ratios, characteristics indicative of larger ice crystals. A conceptual model for mixed particle ensembles was developed and used with theoretical calculations and available meteorological data to demonstrate systematic PSC evolution induced by rapid adiabatic cooling. SAM II PSC sightings during January 1989 were more numerous than those in all but one of the previous 10 years of observation. PSCs were observed by SAGE II from January 31-February 2 near the edge of (or even outside) the polar vortex (near  $50^\circ\text{N}$ ), where there was extensive sunlight and, hence, an increased likelihood of chlorine-catalyzed ozone loss. This unusual episode was forced by a southward displacement of the vortex, with the vortex edge overrunning a strong mid-tropospheric ridge and producing rapid adiabatic cooling to temperatures below the PSC threshold.

E. JOURNAL PUBLICATIONS.

Kent, G. S., Poole, L. R., McCormick, M. P., Schaffner, S. K., Hunt, W. H., and Osborn, M. T.: Optical backscatter characteristics of Arctic polar stratospheric clouds, *Geophys. Res. Lett.* 17, 377-380, 1990.

McCormick, M. P., Kent, G. S., Hunt, W. H., Osborn, M. T., Poole, L. R., and Pitts, M. C.: Arctic Polar Stratospheric Cloud Observations by Airborne Lidar, *Geophys. Res. Lett.* 17, 380-382, 1990.

Osborn, M. T., Poole, L. R., and Wang, P.-H.: SAM II and lidar aerosol profile comparisons during AASE, *Geophys. Res. Lett.* 17, 401-404, 1990.

Osborn, M. T., Pitts, M. C., Powell, K. A., and McCormick, M. P.: SAM II aerosol measurements during the 1989 AASE, *Geophys. Res. Lett.* 17, 397-400, 1990.

Pitts, M. C., Poole, L. R., and McCormick, M. P.: SAGE II observations of polar stratospheric clouds near 50N, January 31-February 2, 1989, *Geophys. Res. Lett.* 17, 405-408, 1990.

Poole, L. R., Kent, G. S., McCormick, M. P., Hunt, W. H., Osborn, M. T., Schaffner, S. K., and Pitts, M. C.: Dual-polarization airborne lidar observations of polar stratospheric cloud evolution, *Geophys. Res. Lett.* 17, 389-392, 1990.

**A Raman Lidar for the Remote Measurement of  
Temperature and Trace Species**

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**Co-Investigators:** Mark R. Schoeberl  
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Leslie R. Lait

This program has a number of scientific objectives associated with understanding the springtime ozone depletions at the poles. Currently the effort is focussed on developing the instrument which is a lidar system to operate on the DC-8 aircraft and make simultaneous measurements of pressure, temperature, methane and water vapor. It is planned to operate this system in conjunction with an ozone measuring lidar. The rationale is that methane can be used as a tracer to distinguish between air from inside the polar vortex and outside air. One needs to know this if one is to explain the mechanism responsible for generating air with reduced ozone levels. The measurements of temperature, pressure, and water vapor content permit the investigation of conditions leading to the formation of PSC's which are a necessary component of the chemical destruction of ozone in the polar spring.

This program was initiated in July, 1991. To date a preliminary detector design has been generated, some parts have been fabricated and other components have been ordered. Many of the components for the system electronics have also been ordered. An RFP for the telescope has been issued and testing of a few of the received components has begun. Under the best of circumstances a system ready for testing could be available by the summer of 1993.

**Earth Science Advanced Aircraft (ESAA) and the Small High-Altitude Science Aircraft (SHASA) Project**

Philip B. Russell (ESAA Team Leader)  
NASA/Ames Research Center

Jennifer L. Bear-Riedhart (SHASA Project Manager)  
NASA/Ames Dryden Flight Research Facility

**Research Objectives**

In 1990, following several years of related activities, NASA Ames established an Earth Science Advanced Aircraft Team to address the following goals:

- Identify optimal ways of applying Ames aeronautical and scientific skills and facilities to the advanced-aircraft needs of the Earth Science community.
- Foster NASA's continuing leadership role in multi-investigator Earth Science aircraft missions.
- Interface optimally with ESAA efforts at other agencies and institutions.
- Develop funded projects to achieve the above goals.

Subsidiary objectives are to:

- Develop advanced-aircraft requirements documents that address the broad spectrum of Earth Science needs and that carry the endorsement of community leaders
- Identify the range of alternatives for meeting the science requirements
- Identify technology requirements
- Define the relationship among costs, capabilities, and science
- Foster feasibility and design studies, and appropriate aircraft developments and flight tests, that lead to required enhancements of the nation's Earth Science aircraft fleet
- Provide enhanced scientific flight opportunities to Ames and other Earth scientists.

**Summary of Progress and Results**

In 1990-91 funding from this task was used to complete a conceptual design study (Reed et al., 1991) for an aircraft intended to meet the consensus requirements defined by a workshop held in Truckee, California in 1989. That workshop, on "Requirements for a Very-High-Altitude Aircraft for Atmospheric Research," made the consensus recommendation (NASA, 1989) that an aircraft be developed with the capability of carrying payloads of 1400 kg (3000 lbs) at subsonic speeds to an altitude of 30 km (100,000 ft) for a range of 10,000 km (6,000 nm).

The concept aircraft, called Stratoplane, was described at the October 1990 Workshop on Lower Stratospheric Measurement Issues, sponsored by the High Speed Research Program (HSRP). At the same workshop Aurora Flight Sciences Corporation described a much

*Biennial Research Summary, 1990-91*  
*Upper Atmosphere Research Program, Aircraft-Borne Measurements*

smaller aircraft, called Perseus A, designed to carry stratospheric research payloads of 50-70 kg (110-144 lb) to altitudes of at least 25 km (82,000 ft) with a range of about 500 km.

Discussions surrounding the workshop talks led to the concept of Perseus A as a first step on the path to more capable aircraft that might eventually approach the capabilities called for by the Truckee report (NASA, 1989). This concept helped to unify elements of the community that had been advocating one or the other types of aircraft

This unification of the community, together with a convergence of the needs of UARP and HSRP and a number of related factors, eventually resulted in the formation of the Small High Altitude Science Aircraft (SHASA) Project to develop and test-fly Perseus A. SHASA is funded by three NASA sources: the Small Business Innovation Research (SBIR) Program, HSRP and UARP. SHASA is managed by the NASA Ames Dryden Flight Research Facility, which will also host the Perseus A flight tests. Ames-Moffett's role in the SHASA Project includes providing personnel with the aeronautical and scientific expertise to assist in the technical oversight of the Perseus A development, especially with regard to propulsion, aerodynamics, payload accommodations, and suitability for mission operations.

The SBIR contract between NASA Ames and Aurora Flight Sciences Corporation for development of the high-altitude engine was signed in May, 1991. At this writing the contract for Perseus A fabrication, assembly, and flight testing, which will be supported by HSRP and UARP funds, is about to enter negotiation, and signing is expected in September, 1991. Engine demonstration is scheduled for 1992 and high-altitude flight tests for 1993. The first science mission involving Perseus A is scheduled for 1993 or 1994.

An AIAA meeting paper (Russell et al., 1991) prepared under this task provides a description of the Perseus A aircraft and how it fits into the larger context of the Earth Science Advanced Aircraft Team's activities to address the broader needs of the many subdisciplines of Earth System Science.

Other ESAA Team activities in 1991 included helping to organize the CalSpace/NASA Ames Workshop on Scientific Application of Remotely Piloted Aircraft Measurements of Radiation, Water Vapor and Trace Gases to Climate Studies (La Jolla, July, 1991), presenting a paper there, contributing to the workshop report, and organizing sessions on "Civilian and Military Mission Needs for Earth System Science" at the Workshop on Civilian and Military Needs for Automated Instrument Platforms in the 1990s and Beyond, to be convened by the Association for Unmanned Vehicle Systems in January 1992.

## **Publications**

Reed, R. D., G. L. Harris, and A. G. Sim, 1991: Stratospheric Surveyor Aircraft "Stratoplane" Design Study. Available from first author, PRC Dryden Research Facility, P.O. Box 273, Building 483, Edwards, CA 93523

Russell, P. B., J. Langford, J. Anderson, D. Lux, D. Hall, and S. Wegener, 1991: Advanced Aircraft for Atmospheric Research. AIAA Paper No. 91-3162, Aircraft Design Systems and Operations Meeting, Baltimore, September 23-25.

## **Reference**

NASA, 1989: Global Stratospheric Change: Requirements for a Very-high-altitude Aircraft for Atmospheric Research. NASA Conference Publication 10041.



## **E. ROCKET-BORNE MEASUREMENTS**



# **Sounding Rocket Studies of CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, and Other Trace Constituents in the Upper Stratosphere and Mesosphere**

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University of Pittsburgh  
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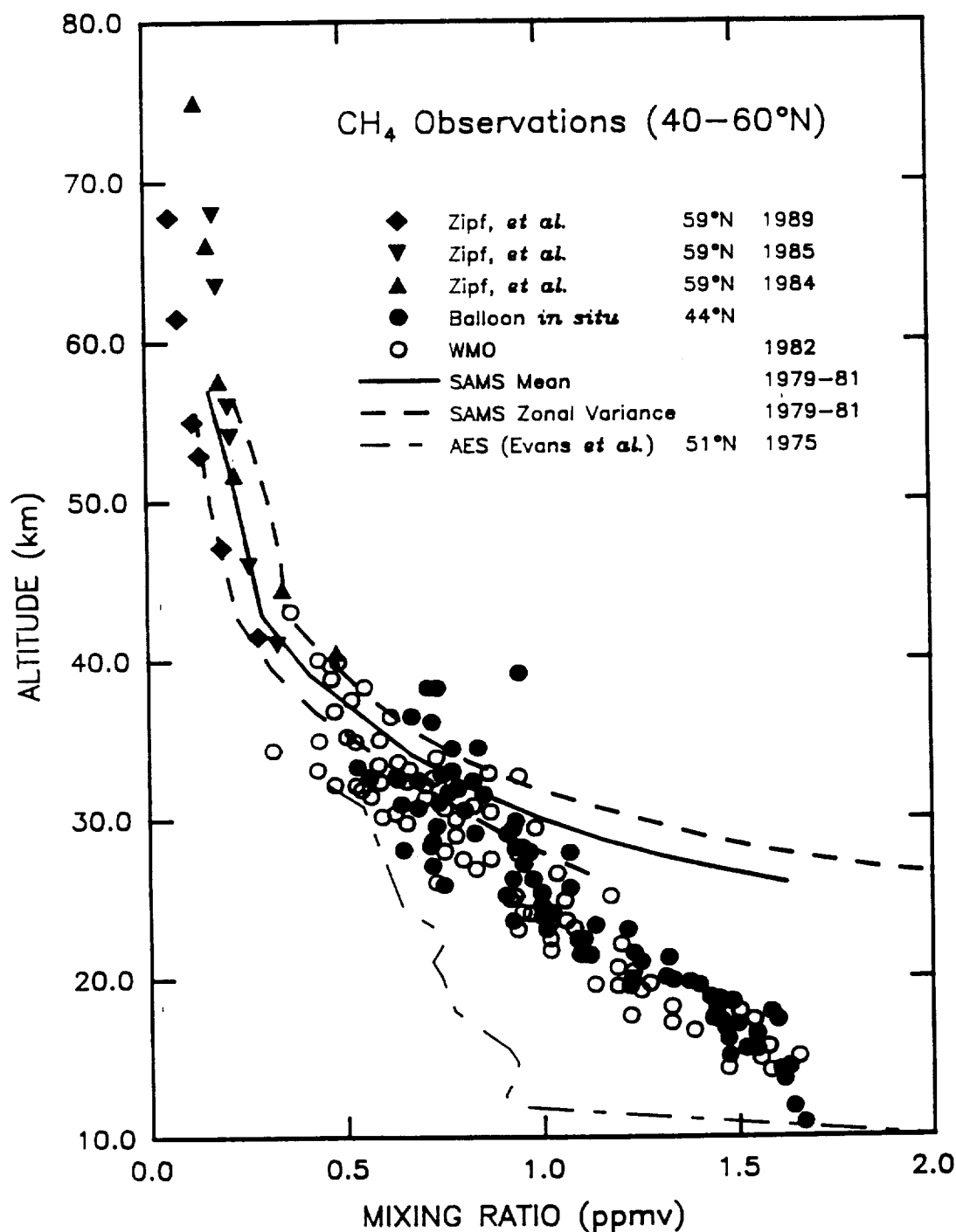
## **ABSTRACT**

A rocket-borne, cryogenic whole-air sampler [CWAS] is used to investigate the sources and sinks of CO<sub>2</sub>, N<sub>2</sub>O, NO, CH<sub>4</sub>, and other minor constituents in the middle atmosphere from 30-80 km. The atmospheric samples are collected on gold-plated surfaces maintained at ~15°K by on-board CTI-8 closed-cycle helium refrigerators. The cold fingers are located in specially prepared stainless steel canisters and are exposed to the atmosphere through pneumatically actuated UHV valves. The CWAS payload collects samples on the upleg of the flight in the ram position. The large samples collected in this manner (~2-15 std-liters) are concentrated further after recovery so that the density of the final samples analyzed by optical, mass spectrometer, and gas chromatographic techniques is ~10<sup>5</sup> times the ambient values. Mixing ratio values with a precision better than ±1% can be obtained by this technique over the entire altitude range with a resolution, Δz, varying from 0.5-3 km. CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O mixing ratio profiles and data on the altitude variation of the <sup>12</sup>C/<sup>13</sup>C, <sup>18</sup>O/<sup>16</sup>O, and <sup>18</sup>O/<sup>17</sup>O isotope ratios in the middle atmosphere have been obtained from Nike-Orion flights launched from the White Sands Missile Range (WSMR) (32°N) and from Churchill Research Range (CRR), Churchill, Manitoba (58°N). During this summary period [1990-1991], CWAS samples obtained in the arctic air mass above CRR following the major solar flare during March 1989 were analyzed, and the CWAS payload was reflown successfully from the Poker Flat Research Range (65°N) on 25 April 1991.

## **PROGRESS REPORT**

The CWAS payload was designed originally to obtain trace constituent data in the altitude range 40-80 km in an effort to study long-term trends in the middle atmosphere at midlatitude and northern sites. As part of this effort, in-situ tests were carried out from 29 km to 110 km in order to determine over what altitude range this technique would provide high accuracy mixing ratio data that would be useful to the UARS Correlative Measurements Program. The field tests indicated that high-quality samples could be obtained over an altitude range from 30-70 km. The CWAS payload was subsequently selected as a member of the CMI team, and the sampler payload is being prepared now for a February 1992 launch from WSMR. Additional work has been done during this summary period to improve our analysis facility so that preliminary mixing ratio results should be available to the UARS science team two week after a CWAS launch.

The samples from fifteen CWAS launches have now been analyzed in detail. Some of the methane results obtained in northern Canada are shown in the figure where they are compared with the body of CH<sub>4</sub> data obtained by earlier balloon and satellite experiments.



The CWAS payload was launched twice from the Poker Flat Research Range during late April 1991 in an effort to obtain high-altitude samples at a northern latitude location near turn around. The first launch took place on 25 April 1991 and successfully collected samples from 45 km to 70 km. The payload was launched a second time five days later but was destroyed when the first stage rocket malfunctioned. A new CWAS payload is being built and will be ready for launch by February 1992 when the CMI program begins.

## Biennial Research Summary

### A. Title: Rocket Temperature Soundings

### B. Investigators and Institutions:

**Francis J. Schmidlin**  
**NASA/GSFC/Wallops Flight Facility**

### C. Abstract:

Rocket-borne measurements of temperature and wind are used; to obtain a better understanding of the processes that control the dynamical behavior of the stratospheric region, to monitor temperature trends, to detect global change, to verify and monitor remote measurements (ground- and satellite-based), to provide direct wind measurements for verification of the balance wind derived from remote measurements, and to provide density measurements for large space vehicle operations.

### D. Progress and Results Summary:

During the period October 1989 through June 1991, sixty-four measurements of temperature and wind were obtained using the Super Loki Datasonde and inflatable sphere rocket instruments. A success ratio of 92 percent was attained, far above that presently obtained at other launch sites. Since resources are limited, launchings are discontinued between May and September. It is necessary that the inventory contain enough flight systems to permit one per week launch capability. Although we use the joint procurement capability in conjunction with the U.S. Air Force, resulting in a much lower per unit cost, funds are insufficient to meet a minimum of the one-per-week-launch objective. The inflatable sphere system costs \$300-\$400 less than the Datasonde, provides accurate temperature and winds, has fewer failures, and when combined with high-altitude balloons (~35-42 km) makes the use of the sphere most cost-effective.

Analysis to study the character and magnitude of stratospheric temperature trends using the rocket data available since 1970 is being carried out. Measurements since 1970 are from a consistent data set because the same instrument type has been used over this time interval at all of the rocket launch ranges, and data are reported in the same format. These attributes increase the confidence of the trend analysis results. The temperature trend since 1970 has been downward, however, before we can fix an accurate value we must consider the results that are obtained from other measurement systems, such as from satellite retrieved temperatures. This involves more work than time and resources permit. Review of the falling sphere technology has found it to provide quite accurate temperature measurements between 85 km and the point of sphere collapse (near 35 km). Density is the basic parameter calculated by solving the equations of motion; radar position data are used. The density value is used to calculate the pressure and ultimately the temperature. Any error resulting in the calculated density appears as a similar magnitude error in pressure, but the error cancels when the gas equation is solved providing an accurate value of temperature. Consequently, a linear error in density does not impact the temperature calculation. The retrieved temperatures are accurate between 35-85 km. as demonstrated theoretically, with computer simulation, and with actual flight comparisons between spheres and Datasondes.

Evaluation of high-altitude balloons (~42 km) is in progress. These balloons will enable a instruments to confidently obtain temperature and wind data (and other parameters, if required) to 38-42 km. The advantages and effect of using such balloons will be discussed in a future report.

#### E. Publications:

Schmidlin, F. J., H. S. Lee, and W. Michel, 1991: The inflatable sphere: A technique for the accurate measurement of middle atmosphere temperatures. Accepted for publication in J. Geophys. Res.

Lee, H. S., F. J. Schmidlin, and W. Michel, 1989: Application of an optimal filter for inflatable sphere data processing. In ESA, European Rocket and Balloon Programs and Related Research. pp 135-138.

Croskey, C. L., L. C. Hale, J. D. Mitchell, F. J. Schmidlin, U. -P. Hoppe, 1990: Electric Field Measurements during the MAC/EPSILON Campaign. J. Atmos. Terr. Phys. Vol 52. pp 1055-1065.

## **F. INSTRUMENT DEVELOPMENT**





## BALLOON-BORNE MEASUREMENTS OF POLAR STRATOSPHERIC OZONE

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Wallops Flight Facility  
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### Research Objectives

The objective of this work is to characterize the vertical distribution of stratospheric ozone over Antarctica during the austral-spring period of ozone depletion.

### Progress and Results

Fifty-five balloon-borne ozonesonde soundings were conducted from Palmer Station, Antarctica (65°S, 64°W), between September 16 and November 13, 1990.

As has been observed in the past, the boundary of the polar vortex moved under the influence of synoptic weather patterns in such a manner that Palmer was within the ozone-depleted region on some days and not on others. During the transitions, the ozone profiles were often strongly layered at the altitudes where ozone depletion was strongest.

Stratospheric ozone depletion was even more severe in 1990 than during the two previous years of maximum depletion, 1987 and 1989. By late September and early October, total column ozone amounts were less than 150 DU when Palmer was within the polar vortex. For comparison, the lowest values observed over the same site during 1987 and 1989 were about 160 DU. The depletion was most severe in the 15-20 km altitude range, where ozone partial pressures reached 5 nb or less.

### Journal Publications

1. Yatteau, John H., Steven C. Wofsy, Ross J. Salawitch, Michael B. McElroy, Mark R. Schoeberl, Leslie R. Lait, Paul A. Newman, Arnold Torres, Torben Jorgensen, William G. Mankin, Michael T. Coffey, Geoffrey C. Toon, Max Loewenstein, James Podolske, Susan E. Strahan, K. Roland Chan, and Michael H. Proffitt, "Effects of Atmospheric Transport on Column Abundances of Nitrogen and Chlorine Compounds in the Arctic Stratosphere," Geophys. Res. Letts., 17, 533-536, 1990.
2. Lait, Leslie R., Mark R. Schoeberl, Paul A. Newman, Michael H. Proffitt, Max Loewenstein, Jim R. Podolske, Susan E. Strahan, K. Roland Chan, Bruce Gary, James J. Margitan, Edward Browell, M. Patrick McCormick, and Arnold Torres, "Reconstruction of O<sub>3</sub> and N<sub>2</sub>O Fields From ER-2, DC-8, and Balloon Observations," Geophys. Res. Letts., 17, 521-524, 1990.

# STRATOSPHERIC OZONE MEASUREMENTS WITH THE ROCOZ-A OZONESONDE

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Chemal, Inc.

Arnold L. Torres  
NASA GSFC/Wallops Flight Facility

## Research Objectives

This work has two objectives. The first is to provide profiles of ozone, pressure, and temperature for comparison with satellite-based ozone measurements. The second is to work with satellite experimenters in conducting the instrument intercomparisons.

## Progress and Results

In the past year we have completed the data set from the ROCOZ-A field campaign at Natal, Brazil, in June/July 1990. This data set is being prepared for publication in the refereed literature, in the same manner as the April/May 1985 ROCOZ-A campaign at Natal, Brazil. A manuscript showing the seasonal cycle for stratospheric ozone from the SBUV satellite instrument at Natal has been prepared for publication. This manuscript is in the review process of the Journal of Geophysical Research. The SBUV manuscript will help explain the expected seasonal differences in stratospheric ozone between the 1985 and 1990 ROCOZ-A campaigns. The results from the 1990 Natal campaign have also been given to the SAGE II instrument team. These data will be the basis for a 1990 ROCOZ-A/SAGE II comparison, similar to the 1985 comparison that has been published in the refereed literature.

## Journal Publications

1. McDermid, I. S., S. M. Godin, R. A. Barnes, C. L. Parsons, A. Torres, M. P. McCormick, W. P. Chu, P. Wang, J. Butler, P. Neuman, J. Burris, R. Ferrare, D. Whiteman, and T. J. McGee, "Comparison of Ozone Profiles from Ground-based Lidar, ECC Balloon Sonde, ROCOZ-A Rocket Sonde, and SAGE II Satellite Measurements," J. Geophys. Res., 95, 10,037-10,042 (1990).
2. Olivero, J. J., and R. A. Barnes, "Satellite Ozone Comparisons: Effects of Pressure and Temperature," J. Geophys. Res., 96, 5091-5098 (1991).
3. Barnes, R. A., L. R. McMaster, W. P. Chu, M. P. McCormick, and M. E. Gelman, "SAGE II and In-Situ Ozone Profiles at Natal, Brazil: A Basis for Comparison with Other Satellite Instruments," J. Geophys. Res., 96, 7515-7530 (1991).

## II. LABORATORY STUDIES

A. REACTION KINETICS AND PHOTOCHEMISTRY

B. SPECTROSCOPY



A. REACTION KINETICS AND PHOTOCHEMISTRY

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## UPPER ATMOSPHERE REACTION RATE MEASUREMENTS

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### RESEARCH OBJECTIVES

The objective of this task is to provide, in as direct a manner as feasible, kinetic and mechanistic information required for photochemical models of the Earth's upper atmosphere. Absolute rate constants for atom-molecule and radical-molecule reactions are measured as a function of temperature and pressure using the technique of flash photolysis-resonance fluorescence (FP-RF). Rate constant measurements and product channel identification are performed for reactions of atoms and radicals with both radical and molecular species using a discharge flow system with collision-free sampling to a mass spectrometer (DF-MS).

### SUMMARY OF PROGRESS AND RESULTS

We completed the first direct study and the first temperature dependent study of the rate of the reaction  $\text{Cl} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO} + \text{HCl}$  (1).  $\text{CH}_3\text{CHO}$  is a product of the atmospheric oxidation of non-methane hydrocarbons and reaction (1) is used in the laboratory as a source of the acetyl radical ( $\text{CH}_3\text{CO}$ ) and, in the presence of  $\text{O}_2$ , as a source of the acetyl peroxy radical ( $\text{CH}_3\text{COO}_2$ ). We find  $k_1 = 6.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , independent of temperature (210 to 343 K) and total pressure (25 to 200 Torr Argon). This result is consistent with previous relative measurements at 298 K and with that expected on the basis of results from our laboratory for reactions of Cl atoms with several oxygenated molecules such as  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ , etc.

Modification of our DF-MS system for photoionization (Lyman- $\alpha$  resonance lamp, 10.2 eV) was completed and the system used to study the reaction  $\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}$  (2) by monitoring the decay of HCO in excess  $\text{O}_2$ . Although the data suggest the possibility of a minimum in the rate constant at 298 K, the data over the range 200 to 398 K can be reasonably fit to the expression  $k_2 = 3.4 \times 10^{-12} \exp(75/T) \text{ cm}^3 \text{ s}^{-1}$ . This represents the first study of the  $\text{HCO} + \text{O}_2$  reaction at temperatures below 298 K appropriate for stratospheric chemistry. Our data are not consistent with an extrapolation of the two previous higher temperature studies. Less extensive data at 298 K for the related reaction  $\text{HCO} + \text{NO} \rightarrow \text{HNO} + \text{CO}$  (3) yields  $k_3 = 1.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , in excellent agreement with previous measurements. These results were presented at the 11th International Symposium on Gas Kinetics (Assisi; September, 1990).

Our discharge flow system was considerably modified to permit detection of atomic species via resonance fluorescence. A brief study at 298 K was made of the reaction  $\text{Cl} + \text{OCIO} \rightarrow 2\text{ClO}$  (4) as a test of our ability to quantitatively measure  $[\text{OCIO}]$  via UV absorption and flow measurements. We observed  $k_4 = 6.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  in good agreement with previous measurements. We also observed (via MS) formation of ClO as a product of reaction (4) and formation of  $\text{Cl}_2\text{O}_3$  as a product of the subsequent reaction  $\text{ClO} + \text{OCIO} \rightarrow \text{Cl}_2\text{O}_3$  (5). A serious OCIO explosion in the laboratory prevented quantitative measurements of this rate constant. Although the major loss process for OCIO in the atmosphere is photolysis, the greatly enhanced level of OCIO observed in the Antarctic spring and its ubiquitous presence in complex laboratory systems (especially ones designed to examine photolysis and reactivity of the ClO dimer) require a sound knowledge of the reactivity of OCIO with species such as Cl, ClO and O.

An extensive DF-RF study of the reaction  $\text{O} + \text{OCIO} \rightarrow \text{ClO} + \text{O}_2$  (6) has been completed over the temperature range 200 to 400 K. At the time this work was initiated, there was only a single study done in 1973 at 298 K. At 298 K, we find  $k_6 = 1.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  independent of pressure from 1 to 5 Torr He. This is much slower than the Bemand et al., 1973 value and reasonably consistent with recent (Colussi, 1990) high pressure data (8 to 800 Torr Argon) extrapolated to zero pressure. The temperature dependence of  $k_6$  at 1.2 Torr He was investigated in a large number of experiments at eight temperatures over the interval 200 to 400 K. The temperature dependence exhibits unusual behavior in that the rate constant increases with increasing temperature from 250 to 400 K ( $k_6^a = 2.5 \times 10^{-12} \exp(-950/T) \text{ cm}^3 \text{ s}^{-1}$ ), but from 200 to 225 K the rate constant decreases with increasing temperature ( $k_6^b = 4.5 \times 10^{-15} \exp(518/T) \text{ cm}^3 \text{ s}^{-1}$  or, as a termolecular rate constant,  $k_6^b = 5 \times 10^{-31} (T/300)^{-1.8} \text{ cm}^6 \text{ s}^{-1}$ ). The pressure dependence observed by Colussi at 298 K and the negative temperature dependence observed here from 200 to 225 K suggests the occurrence of the additional process  $\text{O} + \text{OCIO} \xrightarrow{M} \text{ClO}_3$ . Our early results on  $\text{O} + \text{OCIO}$  were reported at the Gas Kinetics Symposium in Assisi (September 1990) and the complete temperature study was presented at the Spring AGU Meeting (Baltimore; June, 1991).

Two systems were studied via DF-MS at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory using tunable VUV radiation as the photoionizing source. In the first, we measured the photoionization spectrum and ionization energy of the hydroxymethyl radical  $\text{CH}_2\text{OH}$ . We had previously measured rate constants for the reaction of  $\text{CH}_2\text{OH}$  with the atmospheric species  $\text{O}_2$ ,  $\text{NO}$  and  $\text{NO}_2$  using electron impact mass spectrometry to monitor  $\text{CH}_2\text{OH}$ . In the NSLS experiments,  $\text{CH}_2\text{OH}$  and  $\text{CH}_2\text{OD}$  radicals were generated in the flow tube by the reaction of F atoms with  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  respectively. We measured  $\text{IE}(\text{CH}_2\text{OH}) = 7.56 \text{ eV}$  and  $\text{IE}(\text{CH}_2\text{OD}) = 7.55 \text{ eV}$ , consistent with photoelectron spectroscopy results. Although  $\text{CH}_3\text{O}$  radicals were also present, the  $\text{CH}_3\text{O}^+$  ion was not detected, in disagreement with the photoelectron spectroscopy results ( $\text{IE} = 7.37 \text{ eV}$ ). However, we did observe the dissociative ionization process  $\text{CH}_3\text{O}^* \rightarrow \text{HCO}^+ + \text{H}_2$  with a threshold at 8.61 eV. This opens up the possibility of studying reactions of the  $\text{CH}_3\text{O}$  radical via DF-MS using the  $\text{HCO}^+$  signal at  $m/e = 29$  to follow  $\text{CH}_3\text{O}$ . In the second system, we attempted to look for primary products (via PIMS) of the reactions of OH with  $\text{C}_2\text{Cl}_4$  and  $\text{C}_2\text{HCl}_3$ . We were particularly interested in the possibility of direct formation of phosgene,  $\text{COCl}_2$ . However, we had problems with generation of OH via the reaction  $\text{F} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{HF}$  and/or survival of OH in the coated flow tube. Either OH and/or  $\text{H}_2\text{O}$  were subject to severe wall loss such that OH never reached the sampling orifice. We have been approved for time on the U-11 beam at the NSLS in the fall of 1991 and intend to continue with work on the products of  $\text{OH} + \text{C}_2\text{Cl}_4$  and  $\text{C}_2\text{HCl}_3$ .

James Gleason completed his tenure as an NAS/NRC Resident Research Associate. Fred Nesbitt (Coppin State College and Catholic University of America) continues as a part time research associate.

#### JOURNAL PUBLICATIONS

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- "A discharge flow - photoionization mass spectrometry study of hydroxymethyl radicals ( $\text{H}_2\text{COH}$  and  $\text{H}_2\text{COD}$ ): Photoionization spectrum and ionization energy," W. Tao, R. B. Klemm, F. L. Nesbitt, and L. J. Stief, *J. Phys. Chem.*, submitted 1991.
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# UPPER ATMOSPHERE RESEARCH: CHEMICAL, PHYSICAL AND OPTICAL PROPERTIES OF ATMOSPHERIC CONSTITUENTS

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## RESEARCH OBJECTIVES

The objectives of this research task are to evaluate, develop, and apply laser-based detection techniques to atoms and molecules that are important in the Earth's upper atmosphere. These techniques are then utilized to measure a variety of chemical, physical, and optical properties: absolute rate constants and product channel distributions for bimolecular reactions; vibrational state distributions and quenching coefficients for excited states; absorption coefficients and photodissociation cross sections. Three techniques that together cover wavelengths from the vacuum ultraviolet to the mid infrared are presently being used - laser photolysis/laser-induced fluorescence, intracavity laser absorption spectroscopy, and color-center laser absorption spectroscopy.

## SUMMARY OF PROGRESS AND RESULTS

A laser photolysis/laser-induced fluorescence (LP-LIF) system that is coupled to a fast-flow system has been assembled and applied to several kinetic and photochemical studies. The atom or molecule of interest can be produced by reaction or excimer-laser photolysis of a suitable precursor and followed by laser-induced fluorescence or resonance fluorescence. Using this system, the photodissociation cross section of OH was measured at 157 nm. The OH radical was produced by titrating the reaction  $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$ ; the photolytically produced H atoms were then detected by resonance fluorescence. The cross section was determined to be  $6.6 \times 10^{-18} \text{ cm}^2$  ( $\pm 25\%$ ). This is in good agreement with the only other experimental determination (Nee and Lee), but represents an improvement of  $\sim 2.4$  in experimental uncertainty; the experimental values are  $\sim 2.2$  higher than the calculated values (van Dishoeck et al.). These results were presented at the 19th Informal Conference on Photochemistry (Ann Arbor; June, 1990) and the 22nd Annual DPS Meeting (Charlottesville; October, 1990 - abstract in B.A.A.S. 22, 1038).

It is now suspected that non-LTE effects may complicate the determination of trace-constituent concentrations by infrared emissions. An example is NO which will be retrieved by CLAES and ISAMS on UARS. We have used the LP-LIF system to provide state-specific information on processes that may contribute to these non-LTE effects. The reaction  $\text{O} + \text{NO}_2 \rightarrow \text{NO}(\nu) + \text{O}_2$  was studied at 298 K to determine the nascent NO vibrational distribution. Using laser-induced fluorescence to probe the NO product, we found that  $\sim 87\%$  of the population was in  $\nu=0$  and  $\sim 13\%$  in  $\nu=1$ . Results of these experiments were presented at the 21st International Symposium on Free Radicals (Williamstown; August, 1991) and a paper is in preparation. Photodissociation of  $\text{NO}_2$  at 351 nm (XeF) produces NO in  $\nu=0$  and 1 with an inverted population. Using this as a source of NO ( $\nu=1$ ), we have made measurements of the temperature dependence of the quenching rate of  $\nu=1$  by Ar,  $\text{N}_2$  and  $\text{O}_2$ . Although preliminary, our results indicate that there is no T-dependence; these experiments are ongoing.

The intracavity laser absorption spectrometer (ICLAS) has been significantly improved with the incorporation of an optical multichannel analyzer that was available in-house. This not only enhances our data acquisition capabilities, but when coupled to a high-voltage pulser, allows us to acquire pulsed as well as quasi-cw signals. The system has been used to investigate absorption by  $\text{H}_2\text{O}$  in weak overtone and combination bands.

A new Nd:YAG laser was acquired and will be used as a photolysis source to generate atoms and radicals that can be detected by the ICLAS system. An extensive model of intracavity laser absorption has been developed to numerically investigate the effects of various physical parameters on this process. In particular, we are formulating an alternative explanation for the wavelength shift and asymmetric lineshapes observed in ICLAS.

We are expanding our detection capabilities to include infrared wavelengths by developing a high-resolution color-center laser absorption spectrometer (CLAS) that covers the range from 2.3 to 3.4  $\mu\text{m}$  with a resolution of  $\sim 1$  MHz. The major components of the system are in place and have been tested by measuring absorptions by  $\text{CH}_4$  ( $\nu_3$ ),  $\text{H}_2\text{O}$  ( $\nu_1$ ),  $\text{CO}_2$  ( $\nu_1 + \nu_3$ ) and  $\text{NO}$  ( $2 \leftarrow 0$ ). Preliminary experiments have also been performed on the latter transition using an intracavity cell to demonstrate extension of ICLAS to infrared wavelengths. First- and second-derivative methods are also being explored to increase detection sensitivity. Additional diagnostic equipment is being added to the CLAS to permit scanning over long wavelengths intervals. When fully operational, the system will be used for kinetic, photochemical and spectroscopic studies. The narrow linewidth of the laser makes this system particularly attractive for measurement of collisional line broadening. In conjunction with our work on  $\text{CH}_4$  ( $\nu_3$ ) absorption, we have also examined the temperature dependence of quenching of  $\text{CH}_4$  ( $\nu_1$ ) emission at 7.8  $\mu\text{m}$  using pulsed infrared excitation of  $\nu_3$  at 3.3  $\mu\text{m}$ . At 298 K we obtained a lifetime-pressure product of 3.5 msec·Torr for quenching by Ar and 1.1 msec·Torr for quenching by  $\text{H}_2$  at 245 K. These pulsed photoacoustic experiments were performed in collaboration with colleagues at York Univ. and the Institute of Space and Terrestrial Science in Canada. Recent analysis of our results have been presented at the 7th International Meeting on Photoacoustic and Photothermal Phenomena (Doorwerth; August, 1991).

As an outgrowth of our work in the infrared, we have also developed a new technique for measuring vapor pressures and monitoring loss processes at low temperatures. In this technique a thin film of material is prepared at low temperature and the change in an infrared absorption of the candidate species monitored as the film is warmed. The technique has been demonstrated for  $\text{CO}_2$  films and subsequently applied to  $\text{C}_2\text{H}_2$ .

Todd Lang is completing his research for his Ph.D. from the U. of MD. Carol Moralejo completed her tenure as an NAS/NRC Resident Research Associate.

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- "Thin-Film Infrared Spectroscopic Method for Low-Temperature Vapor Pressure Measurements," R. K. Khanna, J. E. Allen, Jr., C. M. Masterson and G. Zhou, *J. Phys. Chem.* **94**, 440 (1990).

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- "Measurements of the methane relaxation times...", R. N. Halthore, J. J. Caldwell, J. E. Allen, Jr., J. A. Burt, K. Yang, and P. Delaney, p. 157.
- "Intracavity dye-laser absorption spectroscopy (IDLAS) for application to planetary molecules," T. M. Lang and J. E. Allen, Jr., p. 168.
- "Vapor pressures of acetylene at low temperatures," C. M. Masterson, J. E. Allen, Jr., G. F. Kraus, and R. K. Khanna, p. 357.
- "Spectroscopy and molecular dynamics - a plenary review," J. E. Allen, Jr., p. 429.

## LABORATORY STUDIES OF CHEMICAL AND PHOTOCHEMICAL PROCESSES RELEVANT TO STRATOSPHERIC OZONE

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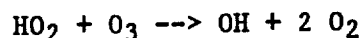
### RESEARCH OBJECTIVES

The purpose of this program is to obtain gas phase kinetic and thermodynamic data for stratospheric processes which will contribute to a better understanding of stratospheric ozone chemistry. We have focussed our efforts in three areas: 1) a mechanistic and kinetic study of the  $\text{HO}_2 + \text{O}_3$  reaction, 2) measurement of rate constants for the reactions of the OH radical with several hydrochlorofluorocarbons and 3) the determination of the nitric acid - water vapor phase diagram at stratospheric temperatures which is central to understanding polar stratospheric cloud formation. The results of these studies will improve models of stratospheric ozone chemistry and predictions of perturbations due to human influences.

### SUMMARY OF PROGRESS AND RESULTS

#### $\text{HO}_2 + \text{O}_3$ Reaction Studies and $\text{HO}_2$ Infrared Spectroscopy

The rate constant for the reaction



has been studied in a discharge flow system with infrared tunable diode laser spectroscopy to monitor  $\text{HO}_2$  and UV laser induced to detect the OH product. We have used isotopic labelling with  $^{18}\text{O}$  to eliminate interference from the back-reaction of OH with  $\text{O}_3$  and to distinguish between H- and O- abstraction channels in the reaction mechanism. We have determined that H- abstraction is the major channel with a branching fraction of  $0.92 \pm 0.05$  at 297 K, and that this ratio increases with decreasing temperature. Thus H abstraction is the dominant mechanism at all atmospherically relevant temperatures and competition between these channels is not responsible for the curvature in the Arrhenius plot as suggested by previous studies. Our direct measurements of the rate constant using the isotopic labelling method at 220 K and 204 K appear to confirm this curvature and indicate a value for the rate coefficient at 200 K which is significantly larger than that extrapolated from the previous NASA data evaluation.

Infrared spectroscopy provides a specific and sensitive method for detecting the  $\text{HO}_2$  radical in laboratory studies and is a potential method for direct measurements in the stratosphere. Quantitative detection of  $\text{HO}_2$  requires knowledge of linestrengths and line positions of individual rovibrational transitions. We have completed our studies of the infrared bands of  $\text{HO}_2$  with a re-analysis of the  $\nu_3$  band. Our revised spectroscopic constants have improved the accuracy for calculating line positions by as much as  $0.2 \text{ cm}^{-1}$  for some higher J transitions.

### OH + HCFC Reaction Studies

Hydrochlorofluorocarbons (HCFC's) are being used as alternatives for chlorofluorocarbons (CFC's) since their higher reactivity with OH in the lower atmosphere limits their transport to the stratosphere and the resultant impact on the ozone layer. We have measured the rate coefficients for the reaction of OH with several propane-based HCFC's in order to evaluate their tropospheric lifetimes and their utility as CFC replacements. The temperature dependence was measured over the range from 295 to 370 K. Extrapolation of the rate coefficient to typical tropospheric temperatures results in lifetimes of 4, 8, and 44 years for HCFC's 225ca, 225cb and 243cc, respectively. The corresponding ozone depletion potentials relative to CFC-11 are approximately 0.02, 0.04, and 0.3, respectively.

### Nitric Acid Trihydrate Vapor Pressure Studies

The importance of heterogeneous chemical reactions on stratospheric aerosol surfaces has been vividly demonstrated by measurements and models of the polar stratosphere. In order to obtain a better understanding of these reactive surfaces we are studying the low temperature thermodynamics of water, nitric acid, sulfuric acid and hydrochloric acid mixtures. The experimental method uses infrared diode laser spectroscopy to continually measure gas phase composition in equilibrium with condensed phases of varying composition. Our initial results have confirmed the earlier work of Hanson and Mauersberger on the formation of nitric acid trihydrate (NAT). We have also observed supersaturations up to a factor of 5 of  $\text{HNO}_3$  vapor relative to NAT equilibrium to occur over pure ice surfaces, which may explain the apparent discrepancy between NAT phase diagram predictions and arctic field observations. We also find evidence for the existence of monohydrate and dihydrate phases although both appear to be metastable with respect to NAT under stratospheric conditions. Future experiments will extend these measurements to HCl and sulfuric acid mixtures, since background sulfuric acid aerosols are believed to provide the nucleation centers for polar stratospheric cloud formation.

These studies are being conducted in collaboration with S. Wofsy and L. Fox from Harvard University.

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## CHEMICAL KINETICS OF THE STRATOSPHERE

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### Objectives

To determine rate constants and product yields of atmospheric reactions by using laboratory kinetics and photochemical techniques, to develop new experimental methods to detect reactive species under conditions occurring in the atmosphere, and to study the physical-chemical properties of atmospheric aerosol surfaces.

### Progress

Reaction probabilities of  $\text{ClONO}_2$  with  $\text{HCl}$  were determined on  $\text{HNO}_3\text{-H}_2\text{O}$  ices of various compositions. The morphologies of water and acid ices were studied by using BET adsorption to determine total surface areas, optical microscopy to determine bulk density and grain size, and infrared spectra to identify the species present. These studies indicate that ices formed by vapor deposition are porous and have large internal surface areas. A theoretical model was developed to describe the interaction of surface reaction and diffusion in porous solids. The theory was tested experimentally and procedures were developed to correct rate data for this effect.

### Publications

1. "Heterogeneous Reactions on Nitric Acid Trihydrate", S. B. Moore, L. F. Keyser, M-T. Leu, R. P. Turco, and R. H. Smith, *Nature* 345, 333 (1990).
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## LABORATORY INVESTIGATIONS OF STRATOSPHERIC HALOGEN CHEMISTRY

Principal Investigator: Paul H. Wine

Collaborators: J. Michael Nicovich, Anthony J. Hynes, R. Peyton Thorn, Edward P. Daykin, Shouzhi Wang, Cornelius A. van Dijk, Christie J. Shackelford, Jeffrey M. Cronkhite, Kevin D. Kreutter, and Jill V. Steidl

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### Research Objectives

The primary objective of this project has been application of state-of-the-art experimental methods to investigate the kinetics, mechanisms, and thermochemistry of gas phase chemical reactions which play important roles in the atmospheric cycles of chlorine, bromine, and iodine. Secondary objectives include contributing to our overall understanding of atmospheric chemistry and chemical reactivity.

### Progress and Results

One focal point of our recent research effort has been the application of chemical kinetics studies to evaluation of free radical thermochemistry. We have characterized the formation-dissociation kinetics and bond dissociation energies of a number of weakly bound adducts of halogen atoms with atmospheric trace gases; species studied include  $\text{ClCS}_2$ ,  $\text{ClCO}$ ,  $\text{ClOO}$ ,  $\text{C}_2\text{Cl}_5$ ,  $\text{BrNO}_2$ , and  $\text{CH}_3\text{S}(\text{Br})\text{CH}_3$ . Also, from studies of the reactions  $\text{Br} + \text{RSH} \leftrightarrow \text{HBr} + \text{RS}$  for  $\text{R} = \text{H}$  and  $\text{CH}_3$ , we have obtained the most precise (and hopefully the most accurate) heats of formation currently available for  $\text{SH}$  and  $\text{CH}_3\text{S}$  radicals.

Other recently completed studies of note include the  $\text{OH} + \text{CH}_3\text{CN}$  reaction and the  $\text{Cl} + \text{CH}_4$  reaction. Using deuterium labeling of hydrogens in the  $\text{OH}$  and  $\text{CH}_3\text{CN}$  reactants, we have demonstrated that adduct formation must be an important channel for the  $\text{OH} + \text{CH}_3\text{CN}$  reaction, that the adduct +  $\text{O}_2$  reaction regenerates  $\text{OH}$ , and that the hydrogen atom which appears in regenerated  $\text{OH}$  is the same one which resided in reactant  $\text{OH}$ . We find that the  $\text{Cl} + \text{CH}_4$  reaction is a little slower than the current NASA panel evaluation suggests at temperatures in the 180-200K range. Our  $\text{Cl} + \text{CH}_4$  results, in conjunction with our recently published low temperature  $\text{Cl} + \text{O}_3$  kinetic data suggest a ratio  $k(\text{Cl} + \text{O}_3) / k(\text{Cl} + \text{CH}_4)$  at 197K of  $1230 \pm 174$ ; although in agreement within combined uncertainties, this ratio is significantly larger than the current NASA panel recommendation of  $859 \pm 481$  or the value  $959 \pm 178$  obtained from a recent relative rate study by DeMore [JGR 96, 4995 (1991)].

Ongoing studies which have yet to yield publishable results include  $\text{BrONO}_2$  photochemistry and  $\text{O} + \text{BrO}$  kinetics. In addition, studies of  $\text{NO}_3$  photochemistry and  $\text{HO}_2 + \text{XO}$  ( $\text{X} = \text{halogen atom}$ ) reaction mechanisms have recently been initiated.

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13. "Use of Deuterium Substitution as a Tool for Investigating Mechanisms of Gas Phase Free Radical Reactions," P. H. Wine, A. J. Hynes, and J. M. Nicovich, in Isotope Effects in Chemical Reactions and Photodissociation Processes, ACS Symposium Series Volume xxx, J. A. Kaye, editor, submitted.
14. "Temperature Dependent Kinetics Studies of the Reactions  $\text{Br} + \text{H}_2\text{S} \leftrightarrow \text{SH} + \text{HBr}$  and  $\text{Br} + \text{CH}_3\text{SH} \leftrightarrow \text{CH}_3\text{S} + \text{HBr}$ . Heats of Formation of  $\text{SH}$  and  $\text{CH}_3\text{S}$  Radicals," J. M. Nicovich, K. D. Kreutter, C. A. van Dijk, and P. H. Wine, *J. Phys. Chem.*, submitted.

# **A MOLECULAR BEAM MASS SPECTROMETRIC STUDY OF THE FORMATION AND PHOTOLYSIS OF ClO DIMER**

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## **RESEARCH OBJECTIVES**

The dimer of the ClO radical has been proposed as a key intermediate in the catalytic destruction of ozone in the antarctic stratosphere. To date, evidence for the existence of this species has come from infrared and ultraviolet spectroscopic observations in laboratory studies. The principal objectives of this research program are the identification of ClO dimer by molecular beam mass spectrometry, the measurement of the rate of formation of the dimer over a wide range of temperatures and pressures, and the elucidation of the photochemistry of the dimer.

## **SUMMARY OF PROGRESS AND RESULTS**

Research performed during this reporting period has included extensive equipment development, a detailed survey of several different chlorine-oxygen systems for the production of ClO, a comprehensive survey of all chlorine-oxygen species produced in these systems under stratospheric conditions, the conclusive mass spectrometric identification and measurements of the rate of formation of the dimer, and preliminary characterization of the adduct Cl<sub>2</sub>O<sub>3</sub>. All of the measurements have been made using molecular beam mass spectrometry (MBMS).

### **Equipment Development**

A set of isothermal flow and static reactors for the investigation of chemical kinetics at typical stratospheric temperatures and pressures were designed, constructed, and tested. These reactors, which were integrated with the MBMS equipment, can be operated at pressures from 0-1 atm and temperatures from ambient to -80 °C. Precise temperature and flow control systems, generators for the several reactants including high concentrations of O<sub>3</sub>, and the adapters needed for the use of laser and arc lamp equipment for experiments involving photolysis were also constructed.



## **Chlorine-Oxygen System Evaluation**

Five chemical systems useful for the generation of ClO were studied. Mass spectrometric and chemical kinetic complications in the use of these systems for studies of the ClO dimer and other species were evaluated. The system in which ClO was produced by the reaction of photochemically generated Cl atoms with O<sub>3</sub> was selected for the dimer measurements.

## **Chlorine-Oxygen Species Survey**

The universal detection capability of MBMS was employed to survey the chlorine-oxygen species produced in these systems at temperatures and pressures relevant to the antarctic stratosphere. It was found that, in addition to Cl<sub>2</sub>O, ClO, ClO<sub>2</sub>, Cl<sub>2</sub>O<sub>3</sub>, and (ClO)<sub>2</sub>, only traces of the high molecular weight species suggested by various investigators were present in any of the systems.

## **Identification and Characterization of ClO Dimer**

The identification of ClO dimer, measurements of its rate of formation, and the determination of its photolysis products and cross section were the major contractual objectives. The unambiguous identification of ClO dimer and the determination of an upper limit for its free energy of formation were completed during this reporting period. Separate measurements have also been made of the rate of formation of ClO dimer based both on the disappearance of ClO and on the appearance of the dimer. Measurements of the cross section and the reaction channels for dimer photolysis have been initiated and should be completed during this contract year.

## **Identification and Characterization of the Adduct Cl<sub>2</sub>O<sub>3</sub>**

The characterization of the adduct formed from ClO and ClO<sub>2</sub> is of importance both in the understanding the behavior of the chlorine oxides in the stratosphere and in making laboratory measurements of the behavior of ClO dimer. This investigation, which included the first mass spectrometric identification of the adduct, showed that significant concentrations of this molecule are present in systems containing ClO and ClO<sub>2</sub>. Since this species could be an important intermediate in the destruction of ozone, future work should include the determination of its photolysis cross section and products.

## **PUBLICATIONS**

The paper, "Molecular Beam Mass Spectrometric Identification of the Dimer of ClO", is being submitted to the Journal of Physical Chemistry. Additional papers on the rate of formation of ClO dimer, the chemistry of the Cl-O system at stratospheric temperatures and pressures, and the characterization of the adduct, are in preparation.

**REACTION RATES OF STRATOSPHERIC GASES WITH AEROSOLS**  
**NASA GRANT W-17,141**

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**Abstract of Research Objectives:**

Heterogeneous reactions of  $\text{N}_2\text{O}_5$  and  $\text{ClONO}_2$  on stratospheric sulfuric acid aerosols may be fast enough to contribute significantly to the global destruction of stratospheric ozone. There are, however, considerable uncertainties in the rates of these reactions, especially their dependence with temperature and composition. The objective of the present research is to determine these reaction rates as a function of temperature, composition and the presence of added HCl. In contrast to all previous studies which employ bulk surfaces, the present research is carried out on real aerosol particles whose size and composition are representative of those in the mid-latitude stratosphere. The resultant gas-phase products and residual reactants are measured in this study by highly sensitive and selective infrared tunable diode laser absorption spectroscopy. The results of this study should thus obviate questions concerning diffusional limitations which may be operative in the bulk studies.

**Summary of Progress and Results:**

Three separate systems have been interfaced and thoroughly tested for these studies: (1) an aerosol generation and characterization system, (2) a low temperature flow reactor system, and (3) an infrared tunable diode laser absorption spectrometer. Part of the first system was used in previous research. However, a considerable number of additions and modifications were necessary to generate and characterize stable monodispersed mixtures of  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  aerosols in a flowing air stream with the proper size and number density for these experiments. A number of tests were carried out to verify the accuracy of measuring the aerosol number density and size distribution in the flow tube, both of which directly impact the overall accuracy of the results.

A low temperature flow reactor system was constructed for these measurements. This system is comprised of a novel stainless steel prereactor section which connects to a glass flow reactor tube. Both have triple walls for low temperature fluid circulation. In measurements carried out to date,  $\text{N}_2\text{O}_5$  from a temperature-controlled trap is passed into the prereactor section. A great deal of attention was devoted to the design of the transfer plumbing to minimize heterogeneous formation of  $\text{HNO}_3$  and  $\text{NO}_2$  from wall decomposition of  $\text{N}_2\text{O}_5$ . The prereactor, which is maintained at the same temperature as the flow tube, contains a movable injector which passes into the flow tube through a sliding seal. A novel crank mechanism allows the injector to be moved in and out of the flow tube without exposing the injector, flow tube, or prereactor to ambient water vapor. The  $\text{N}_2\text{O}_5$ , moreover, is passed into the flow tube through the same length of tubing regardless of the injector position. These features were found to be essential in obtaining high quality data.

In a typical heterogeneous experiment, the residual  $\text{N}_2\text{O}_5$  concentration exiting the flow tube was measured by tunable diode laser absorption spectroscopy (TDLAS) as a function of the injector position. To accomplish this, the  $\text{N}_2\text{O}_5$  was first thermally decomposed to  $\text{NO}_2$  and  $\text{NO}_3$ , and the latter was further reacted with  $\text{NO}$  to form additional  $\text{NO}_2$ . Initially, the  $\text{N}_2\text{O}_5$  concentration was determined by measuring the  $\text{NO}_2$  concentration produced from this converter. However, detailed tests revealed significant systematic errors associated with this procedure due to a changing background  $\text{NO}_2$  concentration from the flow tube and injector inlet. Measurements of  $\text{N}_2\text{O}_5$  are now being carried out by measuring the  $\text{NO}$  consumed in the converter by TDLAS. Both measurements and modelling studies reveal that the conversion process is both linear, constant, and independent of the background  $\text{NO}_2$  concentration and the presence of other species like  $\text{HNO}_3$ . In addition to  $\text{NO}$ ,  $\text{H}_2\text{O}$  from the flow tube is simultaneously measured by TDLAS. This is important in the determination of aerosol composition. All the necessary software for reducing the TDLAS data as well as decay data have been written and thoroughly tested and is routinely being employed.

A number of experiments for  $\text{N}_2\text{O}_5$  on  $\text{H}_2\text{SO}_4$  aerosols have been carried out over a range of flow tube pressures (385 Torr to 615 Torr), temperatures (230 K to 296 K), and aerosol compositions (40% to 84%  $\text{H}_2\text{SO}_4$  by weight). The data suggest that the reaction probability is independent of composition, as has been found in other studies. The reaction probability falls in the range between 0.084 and 0.090 for temperatures in the range between 279 K and 296 K, in agreement with previous results by Mozurkewich and Calvert at 296 K but lower than their results at 274 K. As the temperature is lowered, the reaction probability increases, falling in the range between 0.14 to 0.17 ( $T = 230$  K) and 0.18 ( $T = 247$  K). These results, which are significantly higher than all but one previous study (Hanson and Ravishankara, reaction probability = 0.10 at  $T = 230$  K), indicate that heterogeneous reactions between  $\text{N}_2\text{O}_5$  and background stratospheric sulfate aerosols may indeed be very important in the global destruction of ozone. This reaction takes on even greater importance because of the enhanced stratospheric sulfate burden from the eruption of Mount Pinatubo.

Experiments are in progress to extend the studies to lower temperatures, to fill in the data more completely over the present temperatures, and to observe potential enhancements due to addition of  $\text{HCl}$ . In the second phase of this research,  $\text{ClONO}_2$  will be studied employing the same equipment and techniques developed here.

#### Journal Publications:

Reaction Probabilities of  $\text{N}_2\text{O}_5$  on Submicrometer  $\text{H}_2\text{SO}_4$  Aerosols Under Stratospheric Conditions, A. Fried, B. Henry, J. G. Calvert, and M. Mozurkewich, EOS Trans. of the 1991 Spring AGU meeting, 72, (17), 81, (1991).

Reaction Probabilities of  $\text{N}_2\text{O}_5$  on Submicrometer  $\text{H}_2\text{SO}_4$  Aerosols Under Stratospheric Conditions, in preparation for submission to JGR

A Novel Prereactor for Low Temperature Flow Kinetic Studies, in preparation for submission to submission to Rev. of Sci. Inst..

# LABORATORY STUDIES OF HETEROGENEOUS PROCESSES IN THE ATMOSPHERE

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## RESEARCH OBJECTIVES

Heterogeneous reactions on the surfaces of polar stratospheric clouds (PSCs) are now recognized to play a central role in the dramatic yearly occurrence of the Antarctic 'ozone hole'. In addition, heterogeneous reactions on normal stratospheric particulate may be important in the global ozone cycle. The goal of this research program is to identify and quantify heterogeneous processes that may have an impact on the stratospheric ozone layer. The surfaces of interest for stratospheric chemistry include ice, concentrated frozen mixtures of nitric acid and ice, and concentrated liquid solutions of sulfuric acid and water.

## SUMMARY OF PROGRESS AND RESULTS

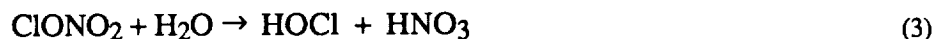
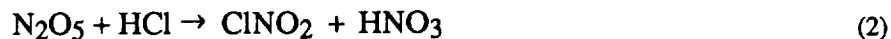
**Characterization of model PSC surfaces.** PSCs are generally classified as type I or type II, depending on their composition and size. Type II PSCs are in the size range 1-100 $\mu$ m and are composed predominantly of water ice. The smaller type I PSCs form at temperatures 5-7°C warmer than the ice frost point and are composed of mixtures of nitric acid in ice. We are using *in situ* Fourier Transform Infrared (FTIR) spectroscopy to study model type I PSC film growth. Model PSC films are grown by dosing calibrated mixtures of nitric acid and water onto an infrared transparent support held at stratospheric temperatures. Film thicknesses,  $d$ , are determined from the optical interference of the infrared radiation using  $d = m\lambda/2\eta$  where  $m$  is a positive integer,  $\lambda$  is the wavelength of light and  $\eta$  is the refractive index of the material.

Film stoichiometries are obtained using temperature programmed desorption (TPD), in which the film is rapidly heated and gaseous  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  are observed mass spectrometrically. After calibrations of the mass spectrometer sensitivity for  $\text{HNO}_3$  and  $\text{H}_2\text{O}$ , ratios of  $\text{H}_2\text{O}/\text{HNO}_3$  in the film are obtained from the relative mass spectrometer signals during film evaporation. Depending on experimental conditions, we are able to make either amorphous solid solutions of nitric acid in ice, or crystalline nitric acid hydrates. TPD experiments have shown that although any concentration of nitric acid is possible for amorphous solutions, there are only three stable crystalline hydrates of nitric acid: nitric acid trihydrate (NAT), nitric acid dihydrate (NAD), and nitric acid monohydrate (NAM).

In addition to measuring the evolved gases during a TPD experiment, we are able to probe the condensed phase in real time during evaporation using FTIR spectroscopy. This results in a so-called temperature programmed infrared (TPIR) curve for each evaporation experiment. The infrared spectra are used to probe for any changes in the crystal structure that occur during annealing and subsequent desorption. TPIR spectra indicate that upon annealing crystalline NAT,

a phase change occurs prior to film evaporation. Crystalline NAD and NAM show no such phase change upon annealing.

**Heterogeneous chemistry on sulfuric acid surfaces.** The heterogeneous reactions (1) through (4) on PSCs have been implicated in the photochemical mechanism now thought to be responsible for the formation of the Antarctic ozone hole. We are currently using a Knudsen cell flow reactor to study these reactions on surfaces that model the background stratospheric sulfate layer to determine their impact on global ozone.



Reactions (1) through (4) all result in the formation of nitric acid. We have measured the solubility of nitric acid in 60-80 wt% sulfuric acid at low temperatures to determine the phase of the product nitric acid. We find that under stratospheric conditions, nitric acid will be formed almost entirely in the gas phase.

We have also measured the reaction efficiencies for reactions (3) and (4) on sulfuric acid surfaces under stratospheric conditions. We find that the reaction efficiency for  $\text{ClONO}_2$  depends strongly on sulfuric acid concentration, and will be relatively low on typical aerosols composed of 75 wt%  $\text{H}_2\text{SO}_4$ . In contrast, the reaction efficiency for  $\text{N}_2\text{O}_5$  is very large, near 0.06, and is nearly independent of sulfuric acid concentration or temperature.

#### JOURNAL PUBLICATIONS

1. "Heterogeneous Reactions on Model Polar Stratospheric Cloud Surfaces: Reaction of  $\text{N}_2\text{O}_5$  on Ice and Nitric Acid Trihydrate," M.A. Quinlan, D.M. Golden, and M.A. Tolbert, *J. Phys. Chem.*, 94, 3255-3260, 1990.
2. "Nitric Acid Uptake by Sulfuric Acid Solutions Under Stratospheric Conditions: Determination of Henry's Law Solubility," C.M. Reihs, D.M. Golden, and M.A. Tolbert, *J. Geophys. Res.*, 95, 16545-16550, 1990.
3. "Fourier Transform Infrared Studies of Model Polar Stratospheric Cloud Surfaces: Growth and Evaporation of Ice and Nitric Acid/Ice," M.A. Tolbert and A.M. Middlebrook, *J. Geophys. Res.*, 95, 22423-22431, 1990.
4. "Characterization of Model PSC films using Fourier Transform Infrared Spectroscopy and Temperature Programmed Desorption," B. G. Koehler, A.M. Middlebrook, and M. A. Tolbert, *J. Geophys. Res.*, *Polar Ozone Issue*, in press.
5. "Heterogeneous Reaction of  $\text{ClONO}_2$  and  $\text{N}_2\text{O}_5$  on Sulfuric Acid Surfaces Representative of Global Stratospheric Particulate," C.M. Reihs, D.M. Golden and M.A. Tolbert, to be submitted to *J. Geophys. Res.*

## HOMOGENEOUS AND HETEROGENEOUS PROCESSES OF ATMOSPHERIC INTEREST

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Collaborators: Leon F. Keyser, Steven B. Moore,  
and Lian T. Chu

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### Research Objectives

The primary objective of this task is to obtain direct measurements of kinetic rate parameters for homogeneous and heterogeneous reactions important in stratospheric chemistry, and to develop new experimental techniques for laboratory study of polar ozone chemistry.

### Summary of Progress and Results

Laboratory activities under this task during 1990 and 1991 concern the heterogeneous chemistry on Type I polar stratospheric clouds. The following studies in kinetics, mathematical model, and infrared spectroscopy were completed:

**Kinetics:** The heterogeneous reactions,  $\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$  (1) and  $\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$  (2), on vapor deposited  $\text{HNO}_3\text{-H}_2\text{O}$  ice substrates were investigated at 196 K by using a fast flow reactor coupled with a quadrupole mass spectrometer. The reaction probability for (1) is  $0.10 \pm 0.02$  and independent of both the  $\text{HNO}_3$  and  $\text{HCl}$  concentrations in the substrate compositions studied. For (2), the reaction probability is approximately  $1 \times 10^{-5}$  near 53.8 wt%  $\text{HNO}_3$ , the composition of pure nitric acid trihydrate, and is about  $1 \times 10^{-3}$  at 46 wt%  $\text{HNO}_3$ . The sticking coefficient of  $\text{HCl}$  on these substrates was also found to be a strong function of the substrate composition, ranging from about  $2 \times 10^{-5}$  at NAT composition to  $6 \times 10^{-3}$  at 45 wt%  $\text{HNO}_3$ .

**Mathematical Model:** The interaction of gas diffusion with surface reaction in porous solids was discussed and applied specifically to heterogeneous rate measurements in flow-tube reactors. External diffusion to the outer surface of a reactive solid, internal diffusion within the pores, surface reaction, and laminar flow were considered. A procedure was developed to correct observed surface rate constants for the interaction of these processes. Measured surface areas and bulk densities were used to construct a semiempirical model for porous diffusion in vapor-formed  $\text{HNO}_3\text{-H}_2\text{O}$  ices which were used to simulate polar stratospheric cloud surfaces. The model was tested

experimentally by varying the thickness of these ices from about 15 to 120  $\mu\text{m}$ . The results are consistent with the model predictions and show that the  $\text{HNO}_3\text{-H}_2\text{O}$  ices used are highly porous, and the internal surface must be considered in calculating kinetic parameters from observed loss rates.

**Infrared Spectroscopy:** Infrared spectra were recorded at 188 K for crystalline mono- and trihydrates of nitric acid formed from vapor deposition. In addition, spectra of fully deuterated forms of these compounds were obtained. These spectra were interpreted in terms of the known ionic structures of the hydrates and the known spectra of oxonium and nitrate ions. Two other less stable solids were formed, a molecular hydrogen-bonded  $\text{HNO}_3\cdot\text{H}_2\text{O}$  complex, stable only at temperatures below 120 or 150 K, and a substance thought to be a crystalline mixture of trihydrate and ice which sometimes formed from water-rich vapors and which upon pumping and/or warming could be converted into crystalline trihydrate.

#### Journal Publications

1. "Heterogeneous Reactions on Nitric Acid Trihydrate", S. B. Moore, L. F. Keyser, M-T. Leu, R. P. Turco, and R. H. Smith, *Nature*, 345, 333 (1990).
2. "Surface Reaction and Pore Diffusion in Flow-Tube Reactors", L. F. Keyser, S. B. Moore, and M-T. Leu, *J. Phys. Chem.* 95, 5496 (1991).
3. "Infrared Spectra of Solid Films Formed from Vapors Containing Water and Nitric Acid", R. H. Smith, M-T. Leu, and L. F. Keyser, *J. Phys. Chem.* 95, 5924 (1991).
4. "Heterogeneous Reactions of Chlorine Nitrate and Hydrogen Chloride on Type I Polar Stratospheric Clouds", M-T. Leu, S. B. Moore, and L. F. Keyser, *J. Phys. Chem.*, in press (1991).
5. "BET Surface Areas and Porosities of Ice Films Formed from Vapors Containing Water and Nitric Acid", L. F. Keyser and M-T. Leu, in preparation (1991).

## PHOTOCHEMICAL AND KINETIC MEASUREMENTS OF STRATOSPHERIC AND TROPOSPHERIC IMPORTANCE

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Collaborators: Robert E. Huie, Renzhang Liu, and Zhengyu Zhang

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### Research Objectives

This task focuses on the elucidation of stratospheric photochemical kinetics through laboratory studies of select chemical reaction systems. Experiments are designed and conducted to determine the temperature and pressure dependencies of rate constants and to infer the mechanisms for those processes important in the modeling of atmospheric chemistry. While the research emphasis is directed towards an assessment of the effects of anthropogenic activity on stratospheric chemical composition, certain predominantly tropospheric reaction systems are also investigated because of their influence on chemical transport to the stratosphere and/or their mechanistic similarities to stratospheric processes. Under this task, the principal investigator also serves as a member of the NASA Panel for Data Evaluation and assists in the annual preparation of a tabulation of evaluated kinetic and photochemical data applicable to atmospheric modeling.

### Summary of Progress and Results

Laboratory activities under this task during 1990 and 1991 fall into the general experimental category of hydroxyl radical kinetic investigations performed using the flash photolysis resonance fluorescence (FPRF) technique. Accomplishments include:

**FPRF:** OH Reaction Kinetics - Temperature dependencies of the rate constants for the reactions with nitroalkanes, ether fuel additives, chlorinated ethenes, and chlorofluoro-ethanes and propanes.

### Journal Publications

1. "The Chemistry of Stratospheric Ozone: Its Response to Natural and Anthropogenic Influences", Int. J. Refrig., **13**, 62 (1990).
2. "The Gas Phase Reactions of Hydroxyl Radicals with a Series of Nitroalkanes over the Temperature Range 240 - 440 K", R. Liu, R. E. Huie, M. J. Kurylo, and O. J. Nielsen, Chem. Phys. Lett. **167**, 519 (1990).
3. "The Atmospheric Reactivity of  $\alpha$ -Methyl-Tetrahydrofuran", T. J. Wallington, W. O. Siegl, R. Liu, Z. Zhang, R. E. Huie, and M. J. Kurylo, Environ. Sci. and Tech., **24**, 1596 (1990).
4. "The Gas Phase Reactivity of OH Radicals with 1,1-Dichloroethene and cis- and trans-Dichloroethene over the Temperature Range 240 - 440 K", Z. Zhang, R. Liu, R. E. Huie, and M. J. Kurylo, J. Phys. Chem., **95**, 194 (1990).



5. "Rate Constants for the Gas Phase Reactions of the OH Radical with  $\text{CF}_3\text{CF}_2\text{CHCl}_2$  (HCFC-225ca) and  $\text{CF}_2\text{ClCF}_2\text{CHClF}$  (HCFC-225cb)", Z. Zhang, R. Liu, R. E. Huie, and M. J. Kurylo, *Geophys. Res. Lett.*, **18**, 5 (1991).
6. "Kinetics and Mechanisms of the Gas Phase Reactions of Peroxy Radicals", T. J. Wallington, P. Dagaut, and M. J. Kurylo, *Chem. Rev.*, submitted for publication (1991).
7. "Rate Constants for the Reaction of OH with HCFC-141b", Z. Zhang, R. E. Huie, and M. J. Kurylo, *J. Phys. Chem.*, submitted for publication (1991).
8. "Heterogeneous Processes: Laboratory and Field Studies", L. Poole, R. L. Jones, M. J. Kurylo, and A. Wahner, *Scientific Assessment of Stratospheric Ozone:1991*, Chapter 3, UNEP and WMO Report.

## LABORATORY STUDIES OF TROPOSPHERIC AND STRATOSPHERIC REACTIONS

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### Objectives

The primary objective of this task is to study the rates and mechanisms of key elementary gas-phase reactions important in stratospheric and tropospheric chemistry. A secondary objective is to utilize high resolution spectroscopic techniques in the ultraviolet, infrared and microwave regions to determine structural parameters and measure line positions and strengths of atmospheric molecules.

### Summary of Progress and Results

In the last two years, work has focused primarily on reactions important in polar ozone depletion. The following studies in kinetics and spectroscopy were completed:

1.  $\text{ClO} + \text{ClO} \longrightarrow \text{Products}$ . Our recent work on the  $\text{ClO} + \text{ClO}$  reaction at low temperatures was extended by studying the reaction at 298 K where disproportionation and termolecular recombination of  $\text{ClO}$ , and thermal decomposition of the  $\text{ClO}$  dimer are all important. In this study, the flash photolysis-ultraviolet absorption technique was used to monitor the disappearance of  $\text{ClO}$  radicals, and the formation of products such as  $\text{OClO}$ . The study provided the first direct measurement of  $k_0^{298}$  at 298 K for several different bath gases, the branching ratios for the  $\text{Cl} + \text{ClOO}$ ,  $\text{Cl}_2 + \text{O}_2$  and  $\text{Cl} + \text{OClO}$  product channels, and the thermal decomposition rate constant for  $\text{ClOOCl}$ .

2.  $\text{O} + \text{OClO} + \text{M} \longrightarrow \text{ClO}_3 + \text{M}$ . The  $\text{O} + \text{OClO}$  reaction was studied over a wide temperature and pressure range using the laser photolysis-resonance fluorescence technique. This study revealed for the first time the presence of a recombination channel which dominates over the bimolecular channel at pressures greater than about 50 torr. The product of the recombination channel is assumed to be symmetrical  $\text{ClO}_3$ , a species not observed previously. The standard enthalpy of formation of  $\text{ClO}_3$  was inferred from the measurement of  $k_0^{298}$  using the theory of Troe and co-workers.

3. Molecular Structure of  $\text{Cl}_2\text{O}_3$ . Submillimeter absorption spectroscopy has been used to determine the molecular structure of  $\text{Cl}_2\text{O}_3$ . This molecule may play an important role in polar ozone chemistry as a temporary reservoir for chlorine. Knowledge of the  $\text{Cl}_2\text{O}_3$  structure is important in establishing thermal and photochemical reaction pathways for this molecule.

4. Kinetics of ClO Dimer Formation. The formation of the ClO dimer is hypothesized to be a key step in the catalytic destruction of O<sub>3</sub> by chlorine-containing compounds in the polar stratosphere. We have studied the mechanism of the ClO + ClO reaction at low temperature using submillimeter spectroscopy to monitor ClO, ClOOCl and OClO to establish the material balance for the reaction. This is important in determining the existence of stable ClO dimer isomers.

#### Journal Publications

1. Sander, S. P., Friedl, R. R. and Yung, Y. L., "Rate of Formation of the ClO Dimer in the Polar Stratosphere: Implications for Ozone Loss", *Science*, 245, 1095 (1989).
2. Anderson, J. G., Brune, W. H., Lloyd, A. A. Sander, S. P., Starr, W. L., Loewenstein, M. and Podolske, J., "Kinetics of O<sub>3</sub> Destruction by ClO and BrO Within the Antarctic Vortex: An Analysis Based on In Situ ER-2 Data", *J. Geophys. Res.*, 94, 11480 (1989).
3. Birk, M., Friedl, R. R., Cohen, E. A., Pickett, H. M. and Sander, S. P., "The Rotational Spectrum and Structure of Chlorine Peroxide", *J. Chem. Phys.*, 91, 6588 (1989).
4. Yung, Y. L., Allen, M., Crisp, D., Zurek, R. W. and Sander, S. P., "Spatial Variation of Ozone Depletion Rates in the Springtime Antarctic Polar Vortex", *Science*, 248, 721 (1990).
5. Colussi, A. J., "Formation and Decay of (<sup>3</sup>P<sub>J</sub>)O Atoms in the Laser Flash Photolysis of Chlorine Dioxide (OClO) at 308 nm", *J. Phys. Chem.*, 94, 8922 (1990).
6. Colussi, A. J., Sander, S. P. and Friedl, R. R., "Thermodynamics of \*Acetylene van der Waals Dimerization", *Chem. Phys. Lett.*, 178, 497 (1991).

## SPECTROSCOPIC STUDIES OF REACTION INTERMEDIATES AND PRODUCTS

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### Research Objectives

This project involves the application of spectroscopy to the study of reaction rates, intermediates and products that are important in the Earth's atmosphere. The experiments are carried out using a high resolution Fourier Transform spectrometer, a linear photodiode array spectrometer, and a monochromator to obtain IR, visible, and UV spectra of transient and stable species of atmospheric importance. Reaction rate coefficients, absorption cross sections, and reaction mechanisms are investigated. The obtained data helps to improve our knowledge of stratospheric chemistry and to provide spectroscopic data for laboratory and field measurements.

### Progress and Results

(a) The UV absorption spectrum of HOCl was measured at room temperature over the wavelength range 200 to 380 nm with a diode array spectrometer. Previous investigations of this system were complicated because HOCl exists in equilibrium with  $\text{Cl}_2\text{O}$  and  $\text{H}_2\text{O}$  and the absorption cross section of  $\text{Cl}_2\text{O}$  in the near UV is greater than that of HOCl. In our study, preferential photolysis of  $\text{Cl}_2\text{O}$  in a mixture of  $\text{Cl}_2\text{O}$  and HOCl was used to enrich the sample in HOCl. Infrared absorption measurements with FTS were used to provide an independent analysis of the sample purity. The UV absorption spectrum peaks at 242 nm with an absorption cross section of  $2.1 \times 10^{-19} \text{ cm}^2$  in excellent agreement with some earlier work. An infrared band intensity of  $230 \text{ cm}^2 \text{ atm}^{-1}$  for the  $\nu_2$  band of HOCl was also determined. These data helps define the chemistry and the lifetime of HOCl in the stratosphere and provides a basis for accurate measurement of HOCl in the stratosphere using IR methods.

(b) The absorption spectrum of  $\text{O}_2$  and  $\text{O}_2\text{-O}_2$  collision pairs were measured over the wavelength range from 330 to 1140 nm using  $\text{O}_2$  pressures up to 55 atm. Absorption cross sections and pressure dependence were measured for bands centered at 343.4, 360.5, 380.2, 446.7, 477.3, 532.2, 577.2, 630.0, 688, 762, and 1065.2 nm. The data obtained are useful in the analysis of trace gas measurements using long path absorption techniques.

(c) The relative intensities of 88 pairs of rovibrational transitions of OH distributed over 16 vibrational bands have been measured in both infrared emission/absorption. The relative intensities provide detailed information about the shape of the OH dipole moment function and hence the absolute Einstein A coefficients. These results will be used in modeling the near infrared and visible atmospheric emission of OH to determine its concentration in the mesosphere.

(d) The  $\nu = 1-0$  band of BrO in the  $3/2$  spin state was measured in absorption. One hundred and thirty transitions were assigned and analyzed to determine improved molecular constants. The  $\nu = 1-0$  band strength was determined to be  $5.04 \text{ cm}^2 \text{ atm}^{-1}$ . The data will be useful for atmospheric and laboratory detection of BrO.

e) The self reaction of BrO was studied using the pulsed photolysis of a mixture of  $\text{Br}_2$  and  $\text{O}_3$ . The temporal profiles of BrO and  $\text{O}_3$  were monitored using a monochromator and a diode array

spectrometer. The rate coefficients for the loss of BrO to give Br<sub>2</sub> and the branching ratio for the formation of Br were measured as a function of pressure and temperature. From this information the rate coefficient for the overall reaction and the branching ratios for the two channels were calculated. At low temperatures, the formation of a new very short lived absorber, tentatively identified as Br<sub>2</sub>O<sub>2</sub>, was detected. Based on the above kinetics and spectroscopic information, a mechanism for the self reaction of BrO was proposed. The obtained information is useful in understanding the stratospheric chemistry of Bromine.

f) The UV absorption spectrum and the absolute cross sections of the ClOO radical was measured using the pulsed photolysis apparatus. The equilibrium constant for the reaction  $\text{Cl} + \text{O}_2 \rightleftharpoons \text{ClOO}$  was measured as a function temperature to obtain the heat of formation of ClOO. The rate coefficient for the reaction  $\text{Cl} + \text{ClOO} \rightarrow \text{Products}$  was measured at various temperatures. Our measurements suggest that ClOO is more weakly bound than previously believed and is in agreement with other very recent data. Our data indicates that this radical, an intermediate in the polar ozone depletion, falls apart very rapidly and is not likely to be involved in any other chemistry. In addition, the formation of this free radical will not interfere with the measurements of the ClO radical in the atmosphere using the resonance fluorescence detection of Cl in air.

### Journal Publications

1. Ultraviolet Absorption Cross Sections of Cl<sub>2</sub>O<sub>2</sub> between 210 and 410 nm, J.B. Burkholder, J.J. Orlando, and C.J. Howard, J. Phys. Chem. 94:687-695, 1990.
2. A Combined Analysis of the  $\nu_1$ ,  $\nu_3$ , and  $2\nu_2$  Vibrational States of the NH<sub>2</sub> Radical Using Fourier Transform Absorption and Emission Data, A.R.W. McKellar, M. Vervloet, J.B. Burkholder, and C.J. Howard, J.Mol. Spec. 142:319-335, 1990.
3. Absorption Measurements of Oxygen Between 330 and 1140 nm, G.D. Greenblatt, J.J. Orlando, J.B. Burkholder, and A.R. Ravishankara, J.Geophys. Res. 95:18577-18582, 1990.
4. H + O<sub>3</sub> Fourier transform infrared emission and laser absorption studies of OH(X<sup>2</sup>π) radical: An experimental dipole moment function and state-to-state Einstein A coefficients, D.D. Nelson, A. Schiffman, D.J. Nesbitt, J.J. Orlando, and J.B. Burkholder, J. Chem. Phys. 93:7003-7019, 1990.
5. Infrared Measurements of BrO (X<sup>2</sup>π 3/2), J.J. Orlando, J.B. Burkholder, A.M.R.P. Bopegedera, and C.J. Howard, J. Mol. Spec. 145:278-289, 1991.
6. High-Resolution Measurements of the Bands of Carbonyl Sulfide Between 2510 and 3150 cm<sup>-1</sup>, A.G. Maki, J.S. Wells, and J. B. Burkholder, J. Mol. Spec. 147:173-181, 1990.
7. The rate coefficient for the termolecular channel of the self-reaction of ClO, M. Troler, R.L. Mauldin III, and A.R. Ravishankara, J. Phys. Chem. 94:4896-4907, 1990.
8. High-Resolution Infrared Spectrum of the  $\nu_1$  band of OClO, J. Ortigoso, R. Escribano, J.B. Burkholder, C.J. Howard and W. J. Lafferty, J. Mol. Spec. 148:346-370, 1991.

# KINETICS AND MECHANISMS OF STRATOSPHERIC CHLORINE RELEASE FROM CHLOROFLUOROMETHYL SPECIES

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## Research Objectives

Laboratory investigations leading to improved understanding of the kinetics and mechanism of Cl atom release from chlorofluoromethanes during stratospheric photooxidation are being conducted. Following photolysis by far UV sunlight, which releases the first Cl atom, the accompanying chlorofluoromethyl photofragment rapidly (submicrosecond) adds O<sub>2</sub>. The ensuing reactions of the resultant peroxy radicals lead to the release of the remaining Cl atoms and other photooxidation products. This research aims to reveal the series of elementary reactions by which this occurs, and their kinetic parameters at stratospheric temperatures and pressures. It also seeks to assess the importance of these reactions with respect to inclusion in mathematical models of the stratosphere that are employed for predictions of O<sub>3</sub> depletion. Flash photolysis with time-resolved mass spectrometry is being used to carry out the kinetic investigations.

## Summary of Progress and Results

The kinetics of the termolecular reaction of CF<sub>2</sub>ClO<sub>2</sub> radicals with NO<sub>2</sub> has been studied by flash photolysis of CF<sub>2</sub>ClBr in the presence of O<sub>2</sub> and NO<sub>2</sub>. The decay of CF<sub>2</sub>ClO<sub>2</sub> radicals was followed via the CF<sub>2</sub>O<sub>2</sub><sup>+</sup> fragment ion detected by an ion counting quadrupole mass spectrometer. The results of a room temperature investigation, published a year ago, have been followed by a recently published study over the temperature range 248-324K and at pressures from 1-10 torr. In the latter study, extensive fitting with the Troe F<sub>c</sub> method was done to establish values of the limiting high and low pressure rate coefficients.

The peroxy nitrates formed in the addition of chlorofluoromethylperoxy radicals to NO<sub>2</sub> are a potential reservoir species for Cl atoms. To evaluate the stability of CF<sub>2</sub>ClO<sub>2</sub>NO<sub>2</sub> and its role as a reservoir we have studied the thermal decomposition of this molecule from 276-289K, and at pressures from approximately 3 torr to 40 torr. The unimolecular decomposition to NO<sub>2</sub> and the peroxy radical is wholly within the fall-off at these conditions. A variational RRKM treatment of the dissociation has been combined with our laboratory data for the reverse association reaction to develop a useful model over a wide range of temperature and pressure. A manuscript describing this work is being prepared.

In these kinetics experiments, with a pinhole interfacing the reactor and the ion source, flow through the pinhole may make a contribution to the observed decay of a reactant. The flow is in the transition between continuum flow and free molecular flow, a situation that is difficult to treat theoretically. A simple interpolation formula from which the flow rate may be readily and accurately calculated was found, permitting facile corrections to the decay for the pinhole flow. A manuscript is in preparation.

The unimolecular elimination of Cl atoms from  $\text{CF}_2\text{ClO}$  and  $\text{CFCl}_2\text{O}$  radicals has been observed at 238K and 298K, and at 4 to 20 torr total pressure by measurement of the rate of formation of the carbonyl halide product in real time. The fragment ion  $\text{CFO}^+$  was found to be specific for the detection of  $\text{CF}_2\text{O}$  and  $\text{CFCIO}$ , and was monitored by time-resolved mass spectrometry in flash photolysis of mixtures of  $\text{CF}_2\text{ClBr}$  or  $\text{CFCl}_3$  with  $\text{O}_2$  and  $\text{NO}$ . The Cl atom elimination reactions are very facile, even at low temperatures. The rate constants were estimated by regression analysis of formation curves of  $\text{CF}_2\text{O}$  and  $\text{CFCIO}$ , and decay curves of  $\text{CF}_2\text{ClO}_2$  and  $\text{CFCl}_2\text{O}_2$  determined in the same experiments. The estimated 298K rate constants are:  $(6.4 \pm 1.4) \times 10^4 \text{ sec}^{-1}$  and  $(1.2 \pm 0.4) \times 10^5 \text{ sec}^{-1}$ , respectively. A manuscript describing these results has been submitted for publication.

Presently, the photodissociation of  $\text{CCL}_2\text{O}$ ,  $\text{CFCIO}$  and  $\text{CF}_2\text{O}$  are being investigated by trapping Cl and F atoms with  $\text{NOCl}$ . Quantum yields for atom formation are being determined.

Investigations of the tropospheric chemistry of halogenated and partially halogenated ethylperoxy radicals derived from suggested substitutes for the chlorofluoromethanes have recently been initiated. Current efforts are on the experimental evaluation of methods for rapid generation of the peroxy radicals.

## **Publications**

Kinetics of the Reactions of  $\text{CF}_2\text{ClO}_2$  Radicals with Nitrogen Dioxide. Steven B. Moore and Robert W. Carr, *J. Phys. Chem.*, 1990, **94**, 1393.

An Investigation of the Temperature and Pressure Dependence of the Reaction of  $\text{CF}_2\text{ClO}_2$  Radicals with Nitrogen Dioxide by Flash Photolysis with Time Resolved Mass Spectrometry. Fuxiang Wu and Robert W. Carr, *Int. J. Chem. Kinetics*, 1991, **23**, 701.

Time Resolved Observation of the Formation of  $\text{CF}_2\text{O}$  and  $\text{CFCIO}$  in the  $\text{CF}_2\text{Cl} + \text{O}_2$  and  $\text{CFCl}_2\text{O} + \text{O}_2$  Reactions. The Unimolecular Elimination of Cl Atoms from  $\text{CF}_2\text{ClO}$  and  $\text{CFCl}_2\text{O}$  Radicals. Fuxiang Wu and Robert W. Carr, submitted for publication.

An Interpolation Formula for Accurate Estimation of Orifice Flow Rates in the Transition Flow Regime. Judy Q. Xiong and Robert W. Carr, to be submitted.

# **LABORATORY CHEMISTRY OF CHLORINE AND FLUORINE COMPOUNDS RELATED TO STRATOSPHERIC OZONE DEPLETION**

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## **Research Objectives**

This task is aimed at characterizing in the laboratory chemical processes which are potentially important in the stratosphere. These studies involve homogeneous gas phase reactions, with measurements of elementary rate constants and photochemical parameters over pressure and temperature ranges which cover polar stratospheric conditions. The systems under study include production of  $\text{Cl}_2$  in the self reaction of the  $\text{ClO}$  radical; production of  $\text{HCl}$  in the reactions of  $\text{HO}_2$  and  $\text{OH}$  with  $\text{ClO}$ ; and ultraviolet spectra of  $\text{ClO}_3$  and  $\text{HOCl}$ .

## **Summary of Progress and Results**

The discharge-flow technique for the measurement of elementary gas phase reaction rate constants has been modified to extend the range of its applicability to atmospheric pressures and to low temperatures. The new technique involves turbulent rather than laminar flow to achieve "plug flow" conditions. The system has been characterized by monitoring the distribution of residence times using tracer pulses, and by flow visualization procedures. The rate constant for the reaction between hydrogen atoms and ozone has been determined in order to test the new technique: the measured value is independent of pressure and agrees well with literature values.

## **Publications**

"Fast Flow Technique up to Atmospheric Pressure for Measurements of Reaction Rate Constants", J.T. Jayne, J.V. Seeley and M.J. Molina, in preparation.



# Ozone Excited States: Production and Atmospheric Reactions

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## Research Objectives

Excited electronic and vibrational states of ozone are produced by the  $O + O_2$  recombination reaction and by direct photoexcitation of ozone. The excited vibrational states of ozone are known to play an important role in the heat budget and in non-thermal radiative transfer in the stratosphere and mesosphere. The excited electronic states of ozone are practically unknown and their roles in the atmosphere have not yet been established. The general objectives of this research are to determine the importance in the atmosphere of the excited states of ozone and to obtain the data needed for developing a chemical kinetics model describing their roles. The immediate goals of this research are to determine the quantum yields of ozone excited electronic states produced by photoexcitation, to determine the nature and identities of these states, to investigate the reactions of the excited states with other atmospheric species, and to investigate possible alternative sources and sinks of odd oxygen.

## Summary of Progress and Results

Shortly before the start of this project, experiments in this laboratory revealed that previously unknown excited electronic states of ozone are produced as the result of photoexcitation of ozone in the Hartley band combined with collisional quenching by  $O_2$ . One conclusion drawn from this result is that the quantum yield of ozone photodissociation in the Hartley band is not unity, as has been assumed in all atmospheric chemistry models, and thus one of our objectives is to determine the absolute quantum yields for the production of excited electronic states. Toward that end, laboratory equipment is being purchased and experiments will start in the near future.

Although the 248 nm KrF laser photon energy is less than the  $O_2$  dissociation energy by about 0.12 eV,  $O_3$  is still produced in the laser irradiation of  $O_2$  at this wavelength (Slanger et al., 1988). The  $O_3$  is produced by two processes: an initiation process and an autocatalytic process. The discovery of the ozone excited electronic states led Slanger (private communication) to conjecture that they may play a role in his laboratory experiments. The idea is that a metastable electronic state of ozone may absorb a laser photon and dissociate into three oxygen atoms to result in net production of odd oxygen. In our laboratory, we have investigated the two  $O_3$  formation processes in pure  $O_2$  and in  $O_2 + N_2$  and  $O_2 + Ar$  mixtures at pressures between 200 and 1600 torr and at temperatures between 298 and 370°K. We have found that the initiation process produces  $O_3$  through chemical reactions between ground state  $O_2$  and excited  $O_2$  in the Herzberg A, A' and c states, which are produced by the photoabsorption of  $O_2$  at 248 nm. The autocatalytic process accelerates the  $O_3$  formation by the photodissociation of vibrationally excited  $O_2(v)$ , which is produced in the photolysis of  $O_3$  following its initial formation. There is no indication that the ozone excited electronic states participate in these processes. Both the  $O_2$  Herzberg states and  $O_2(v)$  may play important roles in the sources and sinks of odd oxygen in the atmosphere.

## Journal Publications

"On the Mechanisms for Odd-Oxygen Formation in the Laser Irradiation of  $O_2$  at 248 nm", Jichun Shi and John R. Barker, *J. Geophys. Res.*, in preparation.

ATMOSPHERIC PHOTOCHEMICAL KINETICS  
464-22-01  
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### Objectives

To conduct laboratory studies of stratospheric photochemistry, including absorption cross sections, photolytic quantum yields, reaction mechanisms, and product distributions.

### Progress

As a follow-on to our study of the chemical and UV spectral properties of the ClO dimer (ref. 1), an upper limit of  $4 \times 10^{-18}$  cm<sup>3</sup> has been placed on the equilibrium constant for the  $\text{ClO} + \text{O}_2 \rightleftharpoons \text{ClO}_2$  reaction at 197 K (ref. 2). The new upper limit is three orders of magnitude below the previous NASA recommendation. The rate constant ratio for the reactions  $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$  and  $\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$  has been measured at stratospheric temperatures (ref. 3), and shown to agree within 15% with current values used in model calculations. Upper limits of  $4 \times 10^{-12}$  and  $1 \times 10^{-15}$  cm<sup>3</sup>/molec.-s have been placed on the rate constants for the reactions  $\text{ClO} + \text{CH}_3\text{O}_2 \rightarrow \text{ClOO} + \text{CH}_3\text{O}$  and  $\text{ClO} + \text{CH}_3\text{O}_2 \rightarrow \text{OClO} + \text{CH}_3\text{O}$ , respectively, at temperatures near 200 K. A mechanism has been proposed (ref. 4) which successfully accounts for the observation by Japanese researchers of O-18 enrichment in stratospheric carbon dioxide.

### Publications

1. "UV Spectrum and Chemical Reactivity of the ClO Dimer", W. B. DeMore and E. T. Roux, J. Phys. Chem. 94, pp.5856-5860, 1990.
2. "Equilibrium Constant for the Reaction  $\text{ClO} + \text{O}_2 \rightleftharpoons \text{ClO}_2$ ", W. B. DeMore, Geophys. Res. Lett. 17, pp. 2353-2355, 1990.
3. "Tests of Stratospheric Models: The Reactions of Atomic Chlorine with O<sub>3</sub> and CH<sub>4</sub> at Low Temperature", W. B. DeMore, J. Geophys. Res. 96, pp. 4995-5000, 1991.
4. "Isotopic Exchange between Carbon Dioxide and Ozone via O(1D) in the Stratosphere", Y. L. Yung, W. B. DeMore, and J. P. Pinto, Geophys. Res. Lett. 18, pp. 13-16, 1991.

A. Title of Research Task

Absolute Absorption Cross Sections of Ozone at 300 K, 228 K and 195 K in the Wavelength Region 185-240 nm

B. Investigators and Institutions

Principal Investigator: K. Yoshino

Co-Investigators: W. H. Parkinson  
D. E. Freeman

Institution: Smithsonian Institution  
Smithsonian Astrophysical Observatory

C. Abstract of Research Objectives

In the wavelength region 185-240 nm, the penetration of solar radiation into the Earth's atmosphere is controlled by photoabsorption of O<sub>2</sub> and O<sub>3</sub>. The transmitted radiation is available to dissociate trace species such as halocarbons and nitrous oxide. Only one measurement of the absorption cross sections of O<sub>3</sub> in this wavelength region has been published in the last twenty years (Molina and Molina, 1986), and those results differ significantly from the earlier work. We have recently measured absolute O<sub>3</sub> absorption cross sections in the 240-350 nm region, (Freeman *et al.*, 1985; Yoshino *et al.*, 1988). We apply these proven techniques to the determination of the absorption cross section of O<sub>3</sub> at 300 K, 228 K and 195 K throughout the wavelength region 185-240 nm.

D. Summary of Progress and Results

The absolute absorption cross section of ozone at fixed wavelengths in the region 184-245 nm have been measured at 295, 228 and 195 K. The fixed wavelengths have been selected from atomic lines of Hg I, Cu I and Cu II. The mercury lamp with thermal control and a special Cu hollow cathode lamp provide suitable atomic line sources. The absorption cross section of ozone in the wavelength region 185-250 nm varies from  $1.15 \times 10^{-17}$  to  $3 \times 10^{-19}$  cm<sup>2</sup>. The optical depths measured were restricted to the range  $\ln(I_0/I) \simeq 0.3-2.0$  to ensure good accuracy. With this restriction, the whole set of cross section measurements can be performed with pressures of O<sub>3</sub> in the range 0.1-11 Torr.

The absolute absorption cross sections of ozone have been measured at 12 wavelengths throughout the region 184-245 nm at 295, 228 and 195 K. The results are listed in Table 1. The published values of Molina and Molina are slightly higher than our present values in this wavelength region.

Continuous cross sections of ozone are also measured in the wavelength region 180-245 nm with a hydrogen continuum light source as background source. Because the vuv radiation destroys ozone molecules, the column density of ozone is

expected to vary during the scanning of the entire wavelength region. However the relative cross sections obtained in the scanning mode are normalized to the absolute cross sections that have been measured accurately at 12 atomic line wavelengths.

Table 1. Absorption cross sections of ozone, in unit of  $10^{-2}\text{cm}^2$

$\lambda$ , nm	$x$	Present*			Molina & Molina	
		295K	228K	195K	298K	226K
184.9	19	6.21[7]	6.23[6]	6.21[6]	6.54	6.44
197.9	19	3.32[4]	3.32[6]	3.28[7]	3.35	3.33
200.0	19	3.12[3]	3.04[4]	3.03[1]	3.15	3.15
204.4	19	3.31[5]	3.34[5]	3.35[3]	3.47	3.49
212.3	19	7.31[2]	7.30[3]	7.34[3]		
216.5	18	1.18[1]	1.18[1]	1.19[2]	1.22	1.24
222.6	18	2.26[3]	2.33[4]	2.28[2]	2.31	2.33
230.3	18	4.38[2]	4.43[3]	4.42[6]	4.66	4.68
235.5	18	6.17[9]	6.18[5]	6.22[7]	6.45	6.48
240.4	18	7.98[8]	8.00[5]	8.02[6]	8.40	8.42
244.2	18	9.42[6]	9.46[8]	9.51[6]	9.72	9.75
249.2	17	1.07[2]	1.07[1]	1.07[1]	1.112	1.121

\*The numbers in the brackets are the estimated error of  $1\sigma$  in the last digit.

#### References:

- Molina, L. T., Molina, M. J. 1986, *Absolute Absorption Cross Sections of Ozone in the 185-350 nm Wavelength Range*, J. Geophys. Res. **91**, 14, 501.
- Freeman, D. E., Yoshino, K., Esmond, J. R., and Parkinson, W. H. 1985, *Absolute Absorption Cross Section Measurements of Ozone*, in *Atmospheric Ozone* ed. C. S. Zerefos and A. Ghazi (Dordrecht: D. Reidel) p. 622.
- Yoshino, K., Freeman, D. E., Esmond, J. R., and Parkinson, W. H. 1988, *Absolute Absorption Cross Section Measurements of Ozone in the Wavelength Region 238-335 nm and the Temperature Dependence*, Space Sci. **36**, 395.

#### E. Journal Publications

None

## **A. A New Atmospheric Ozone Source**

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## **C. Research Objectives**

The experimental part of the program has been directed towards an improved understanding of ozone photochemistry, as related to upper atmospheric issues. Apart from the well-publicized Antarctic ozone hole, there are other discrepancies that are found between what modelers predict for the ozone altitude profiles, and what is actually observed. At present, there is an excess amount of ozone in the upper stratosphere and lower mesosphere at temperate latitudes compared to modeling predictions, amounting to 20-50%. This is obviously a consequence of either an underestimation of sources, or an overestimation of losses. We have pursued the former hypothesis, and have shown that the role of vibrationally excited oxygen may be crucial in the photochemistry of the upper stratosphere.

## **D. Progress and Results**

The work carried out in 1990-1991 has continued to involve the question of the role of vibrationally excited oxygen in stratospheric photochemistry, and we can report three major accomplishments.

- (1) We have evaluated the vibrational distribution of oxygen that is generated from ozone photodissociation at 248 nm. This distribution is one of the two critical factors in determining the efficiency of the hypothesized mechanism as an atmospheric ozone source. We find a bimodal distribution, with a first maximum at  $v \sim 8$ , followed by a minimum at  $v \sim 15$ , and then a second maximum at  $v > 22$ . These latter very high  $v$  levels are of particular interest, since their photodissociation can take place in the visible spectral region, where solar flux intensities are very high. The second critical parameter, the rate of quenching of vibrationally excited oxygen by oxygen, is currently being measured.
- (2) The laboratory experiments, reported in Science in 1988, had indicated that ozone production through the mediation of vibrationally excited oxygen takes place by both discrete and continuum absorption. The latter was somewhat surprising, and we decided that it was important to understand the nature of the process and its possible relevance to the atmospheric issues. For this purpose a set of calculations was carried out to determine whether absorption in the Schumann-Runge continuum of oxygen might be responsible for the observed effect. These calculations were performed for oxygen in the  $v = 12-20$  vibrational level range, appropriate to the process at 248 nm. Such calculations had not previously been done for  $v > 2$ . We learned that for an

optically thin system, Schumann-Runge band absorption should be much stronger than continuum absorption, but that for a variety of reasons, in the experimental system the effects should be of similar magnitude, as observed. We therefore believe that we have greatly improved our understanding of the experimental system and how it relates to the atmospheric process.

- (3) Having a source of vibrationally excited oxygen, we have taken the opportunity to make high resolution measurements of the predissociation linewidths for the important  $v=0$  level of the oxygen  $B^3\Sigma_u^-$  state. Because this level is not normally accessible in absorption measurements, its linewidth has never been determined, and yet it is quite important, for a variety of applications, to make such a measurement. The rotational-level-dependent values that we find lie in the  $0.15\text{-}0.4\text{ cm}^{-1}$  range, substantially greater than current theoretical estimates.

## E. Published Papers

- T. G. Slanger and G. E. Gadd, "Formation of Ozone by Irradiation of Oxygen at 248 nm" (response to comments by D. E. Freeman, et al.), *Science* **250**, 1432 (1990).
- R. P. Saxon and T. G. Slanger, "Relative Contributions of Discrete and Continuum Absorption to the Photodissociation of Vibrationally Excited  $O_2$  [ $v = 12\text{-}20$ ]," *J. Geophys. Res. (Atm.)* [Sept. 1991].
- H. Park, P. C. Cosby, R. A. Copeland, and T. G. Slanger, "Predissociation Linewidths for  $O_2(B^3\Sigma_u^-, v=0)$ ," *J. Chem. Phys.* (in preparation).
- H. Park and T. G. Slanger, " $O_2$  Vibrational Distribution from Photodissociation of Ozone at 248 nm", *J. Chem. Phys.* (in preparation).

## STUDY OF THE ATMOSPHERIC CHEMISTRY OF NO<sub>y</sub> SPECIES

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### Abstract of Research Objectives.

The project, concerned with improving our understanding of the behavior of oxidized nitrogen species in the atmosphere involves studies of kinetics and mechanisms of reactions of the oxides of nitrogen (NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>) and of related NO<sub>y</sub> species (HO<sub>2</sub>NO<sub>2</sub>, CH<sub>3</sub>COO<sub>2</sub>NO<sub>2</sub>). The experimental approaches used encompass such techniques as laser induced fluorescence (LIF), FTIR product measurement, NO-O<sub>3</sub> chemiluminescence (C-L), discharge-flow, pulsed laser photolysis, and CW photolysis.

### Summary of Progress and Results.

- i) The rate coefficient for the reaction  $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$  has been measured between 273 and 313 K using UV-visible absorption for the detection of NO<sub>2</sub> and C-L detection of NO.
- ii) The rate coefficient for the reaction  $\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$  has been measured between 223 and 400 K using discharge-flow with detection of NO<sub>3</sub> by LIF, or detection of NO by C-L. The results support a smaller value of the rate coefficient than had been previously recommended.
- iii) A pressure-dependent study of the reaction  $\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$  has been conducted from 236 to 358 K using pressures between 0.5 and 8 torr. The results represent the first measurement of this rate coefficient under conditions pertaining to the middle stratosphere. The results were combined with previous measurements at different pressures and temperatures to refine the fall off parameters for this reaction.
- iv) FTIR was used to study the products arising from the reaction  $\text{NH}_2 + \text{O}_2$ . An upper limit of  $6 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was established for the rate coefficient of this reaction, almost three orders of magnitude smaller than implied from previous, direct measurements.
- v) A product study of the reaction of HO<sub>2</sub> with NO<sub>2</sub> was carried out, in order to obtain an upper limit for the bimolecular channel  $\text{HO}_2 + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2$ . By quantitative detection of HO<sub>2</sub>NO<sub>2</sub> and HONO, an upper limit of  $3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  could be assigned. This is an order of magnitude less than previously thought, and rules out the importance of this reaction in the atmosphere.
- vi) A study has been carried out on the mechanism of PAN decomposition, specifically the proposed reaction  $\text{CH}_3\text{COO}_2\text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2 + \text{CO}_2$ . It has been shown that the distribution of the observed products CH<sub>3</sub>ONO<sub>2</sub> and HCHO can be entirely explained by known free radical chemistry following the dissociation of PAN into CH<sub>3</sub>COO<sub>2</sub> and NO<sub>2</sub>.
- vii) Experiments are in progress to measure the quantum yields for NO<sub>2</sub> photolysis as a function of wavelength (385-420 nm) using NOCl for actinometry. This will be achieved by CW dye laser photolysis. The NOCl cross sections have been measured at temperatures between 223 and 323 K, and found to have a pronounced temperature dependence around 400 nm, where the photolysis experiments will be carried out.
- viii) Experiments are in progress to measure the wavelength-dependence of the quantum yields of O atoms from NO<sub>3</sub> photolysis, using discharge flow production of NO<sub>3</sub> with laser flash

photolysis and resonance fluorescence detection of O atoms. Relative quantum yields have already been determined, which will be put on an absolute basis using the photolysis of O<sub>3</sub> to generate known concentrations of O atoms at selected wavelengths.

ix) Data have been taken from 253 to 323 K, at total pressures between 0.3 and 3000 torr, on the thermal decomposition reaction  $\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$ . A cell has been constructed to allow temperature-dependent measurements up to 20000 torr. Combination of the data on the forward and reverse reactions will then provide constraints on  $F_c$  for the reaction pair and on the equilibrium constant.

#### Journal Publications

The rate coefficient for the reaction  $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$  from 273 to 313 K, C.A. Cantrell, R.E. Shetter, A.H. McDaniel and J.G. Calvert, *J. Geophys. Res.* 95 (1990) 20531-20537.

The NO<sub>3</sub> radical decomposition and NO<sub>3</sub> scavenging in the troposphere, J.A. Davidson, C.A. Cantrell, R.E. Shetter, A.H. McDaniel and J.G. Calvert, *J. Geophys. Res.* 95 (1990) 13963-13969.

Rate coefficient for the reaction  $\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$  between 223 and 400 K, G.S. Tyndall, J.J. Orlando, C.A. Cantrell, R.E. Shetter and J.G. Calvert, *J. Phys. Chem.* 95 (1991) 4381-4386.

Temperature and pressure dependence of the rate coefficient for the reaction  $\text{NO}_3 + \text{NO}_2 + \text{N}_2 \rightarrow \text{N}_2\text{O}_5 + \text{N}_2$ , J.J. Orlando, G.S. Tyndall, C.A. Cantrell and J.G. Calvert, *J. Chem. Soc. Faraday Trans.* 87 (1991) 2345-2349.

An upper limit for the rate coefficient of the reaction of NH<sub>2</sub> radicals with O<sub>2</sub> using FTIR product analysis, G.S. Tyndall, J.J. Orlando, K.E. Nickerson, C.A. Cantrell and J.G. Calvert, in press, *J. Geophys. Res.*

#### In preparation

Temperature-dependent absorption cross sections for NOCl in the 390-650 nm range

Upper limit for the reaction  $\text{HO}_2 + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2$

Unimolecular decomposition of N<sub>2</sub>O<sub>5</sub>

FTIR product study of the decomposition of peroxy acetyl nitrate



## B. SPECTROSCOPY



NASA Upper Atmosphere Research Program: 1990-91 Research Summary

**Title:** Inelastic Collision Processes in Ozone and their Relation to Atmospheric Pressure Broadening

**Principal Investigator:** J.I. Steinfeld  
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**Collaborating Investigators:** M. Spencer, C. Chackerian, Jr.  
NASA Ames Research Center  
Moffett Field, Calif. 94035

**Abstract of Research Objectives:**

The goal of this research project is to identify the contributions of inelastic collision processes to pressure broadening of the ozone infrared spectrum. Knowledge of air-broadening parameters, including temperature dependence, is required for the inversion of atmospheric spectra to obtain total column densities and altitude profiles of trace species. Currently available models for predicting these parameters depend on assumptions about the broadening mechanisms which are tested in this research program. We use an infrared-infrared double-resonance (IRDR) technique in two types of experiments: three-level experiments which directly measure total relaxation rates into or out of a specific energy level, and four-level experiments which indicate energy transfer pathways and which will be used to develop rotational relaxation models. Additional experiments take advantage of the high resolution of the diode laser spectrometer to study ozone self-broadening in the congested  $\nu_3$  band.

**Summary of Progress and Results**

Room temperature self-relaxation rates have been measured in both the ground and vibrationally excited states of ozone by IRDR. Preliminary results were reported in a short communication (Ref. 1), including the V-V transfer rate between the  $\nu_3 = 1$  and  $\nu_1 = 1$  levels and total rotational relaxation rates for four  $\nu_3 = 1$  and three ground state levels.

High resolution spectra were recorded to measure ozone self-broadening. A recent paper (Ref. 2) reports self-broadening coefficients for 15 transitions in the  $\nu_3$  band. These experiments complement the work being carried out at NASA's Ames and Langley Research Centers in filling out the data base of experimental pressure-broadening

coefficients. Self-broadening coefficients were measured for a number of transitions corresponding to those measured in the IRDR experiments so that direct comparisons could be made. It was found that the average of the relaxation rates for the upper and lower levels accounts for only about two-thirds of the total broadening rate, indicating significant contributions from elastic dephasing processes. Similar behavior has now been observed in other systems (Ref. 3).

Recently, IRDR experiments have been conducted using a variety of ozone/foreign gas mixtures representing likely atmospheric collision partners: nitrogen, oxygen, and rare gases. We have made a number of these measurements over the 200 - 300 K temperature range. Analysis of these experiments is nearly complete and a manuscript describing the temperature and collision-partner dependence of the rotational relaxation rates is now in preparation (Ref. 4). These IRDR experiments will also be directly compared with the low temperature nitrogen- and oxygen-broadening measurements being conducted at the NASA Ames Research Center (Ref. 5).

Four-level IRDR experiments have been conducted, probing a variety of rotational levels in the  $v_3 = 1$  vibrational state. In the coming year, we will be analyzing these double-resonance data with the aid of a master-equation relaxation model to obtain state-to-state rotational relaxation rates for the purpose of testing current theoretical models for relaxation and pressure-broadening.

## **Publications**

1. C. Flannery, Y. Mizugai, J.I. Steinfeld, and M.N. Spencer, *J. Chem. Phys.* **92**, 5164 (1990).
2. C. Flannery, J.J. Klaassen, M. Gojer, J.I. Steinfeld, M. Spencer, and C. Chackerian, Jr., *J. Quant. Spectroscopy Rad. Transfer* **46**, 73 (1991).
3. J.I. Steinfeld, P. Ruttenberg, G. Millot, G. Fanjoux, and B. Lavorel, submitted to *J. Phys. Chem.*
4. C. Flannery and J.I. Steinfeld, "Temperature and Collision-Partner Dependence of Rotational Relaxation Rates in Ozone" (manuscript in preparation).
5. M. Spencer, C. Chackerian, Jr., and C. Flannery, "Temperature Dependence of Nitrogen-Broadening Coefficients for Ozone Infrared Transitions" (manuscript in preparation).

**Title: Quantitative Infrared Spectroscopy of Minor Constituents of the Earth's Atmosphere**

**Investigators and Institution:**

C. Chackerian, Jr. (P.I.), L. P. Giver, M. N. Spencer and D. Goorvitch.  
NASA Ames Research Center, Moffett Field, CA 94035-1000.

**Abstract of Research Objectives:**

We make quantitative laboratory spectroscopic measurements of molecular constituents which are of importance in understanding the "health" of the Earth's atmosphere, and emphasize those species which are important for understanding stratospheric kinetics or are used for long term monitoring of the stratosphere. Our measurements provide: (1) line and band intensity parameters which are needed to (a) establish limits of detectability for as yet unobserved species and (b) quantify the abundance of those species which are observed, (2) line positions, half widths and pressure induced shifts are all needed for remote sensing techniques, and (3) data on the above basic molecular parameters at temperatures and pressures appropriate for the real atmosphere.

**Summary of Progress and Results:**

(1) The temperature dependence has been determined for the N<sub>2</sub> broadening of 18 transitions in the  $\nu_3$  band of ozone in the temperature range 180 K to 296 K. (2) A generalized Herman-Wallis treatment is being employed to determine the absolute rovibrational intensities of the ground electronic state of OH. To this end the numerical rovibrational wavefunctions have been computed from the solution of close-coupled radial Schrodinger equations and relative intensity measurements have been obtained with the FTS instruments at Kitt Peak (M. Abrams and S. P. Davis, U. C. Berkeley) and Orsay, France (A. Benidar, R. Farrenq, and G. Guelachvili, U. Paris). (3) The strongest feature in the room temperature infrared spectrum of CH<sub>3</sub>Cl, the RQ<sub>0</sub> branch at 1458.5 cm<sup>-1</sup>, has been modelled on a line by line basis including collisional line mixing ( with N. Lacome, U. Paris, and L. Brown, J. P. L.). (4) Absolute line intensities of the CO<sub>2</sub> band at 720 cm<sup>-1</sup> have been determined from spectra obtained at the Kitt Peak FTS. The line intensities are about 2% smaller than results obtained at NRC (J. Johns, Canada) with a BOMEM FTS. (5) The 30 cm low temperature (60 K - 296 K) absorption cell has been completed, tested and integrated with the BOMEM FTS.

## Journal Publications (1990-1991):

1. C. B. Suarez, C. Chackerian, Jr., F. P. J. Valero, "Recent High Resolution Laboratory Determinations of Line Broadening and Intensity Parameters:  $\text{PH}_3$ ,  $\text{CH}_3\text{D}$  and  $\text{CO}_2$ ", in First International Conference on Laboratory Research for Planetary Atmospheres, Bowie State University, Maryland, Oct. 1989. In NASA Conference Publication **3077**, 74-78 (1990).
2. C. Chackerian, Jr., D. Goorvitch and L. P. Giver, " $\text{N}_2$ -Broadening In the  $\text{HCl}$  Vibrational Fundamental: Temperature Dependence Between 160 and 296K", *J. Quant. Spectrosc. Radiat. Transfer* **43**, 127 (1990).
3. A. Levy, N. Lacombe and C. Chackerian, Jr., "Chapter V, Collisional Line Mixing" in Spectroscopy of the Earth's Atmosphere and Intestellar Molecules (K.Narahari Rao and A. Weber, Eds.) Academic Press Inc. (in press).
4. M. N. Spencer and C. Chackerian, Jr., "Nitrogen Broadening of Ozone  $\nu_3$  Rovibrational Transitions at 220 K", *J. Mol. Spectrosc.* **146**, 135 (1991).
5. A. Benidar, R. Farrenq, G. Guelachvili, and C. Chackerian, Jr., "Anomalous Rovibrational Intensities in the  $\Delta V = 1$  Bands of  $\text{SH}$  ( $X^2\Pi$ )", *J. Mol. Spectrosc.* **147**, 383-391 (1991).
6. C. Flannery, J. J. Klaassen, M. Gojer, J. I. Steinfeld, M. Spencer and C. Chackerian, Jr., "Measurement of Self-Broadening of the Ozone Transitions", *J. Quant. Spectrosc. Radiat. Trans.* **46**, 733-780 (1991).
7. L. P. Giver and C. Chackerian, Jr., "Rovibrational Intensities for the  $(31^{10})_{IV} \leftarrow (00^00)$  Band of  $^{12}\text{C}^{16}\text{O}_2$  at  $4416\text{ cm}^{-1}$ ", *J. Mol. Spectrosc.* **148**, 80-85 (1991).
8. M. N. Spencer, C. Chackerian, Jr., and C. Flannery, " Temperature Dependence of Nitrogen Broadening of Ozone  $\nu_3$  Rovibrational Transitions", *Spectrochimica Acta A* (submitted).

# UV Absorption Cross Section Measurements of Hydrochlorofluorocarbons

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## Objective

To obtain accurate data for gas phase absorption cross-sections for alternative (replacement) compounds for chlorofluorocarbons in the near uv wavelength region is of importance to the NASA Upper Atmosphere Research Program in order to quantify the chlorine release from (and ozone depletion potentials for) such replacement compounds in the stratosphere.

## Summary of Progress and Results

Cross sections in the near uv wavelength region are often very low and measurements are then difficult and unreliable. We have found that absorption cross sections derived from measurements in the liquid phase can, with appropriate correction factors, be converted into accurate gas phase values. Also, because of the higher density of the liquid phase the long wavelength measurements extend well beyond those of the gas phase. Thus a reliable experimental technique is available for determining gas phase absorption cross sections of diffuse absorbers in regions of very low absorptions. Alternative CFC replacement compounds studied so far include HCFC-225ca and HCFC-225cb. Measurements will be continued to include a number of other HCFC's, and additional measurements will be made of the temperature dependence on both gas and liquid phase samples as well.

## Publications

UV Gas and Liquid Phase Absorption Cross Section Measurements of Hydrochlorofluorocarbons HCFC-225ca and HCFC-225cb, W. Braun, A. Fahr, R. Klein, M. J. Kurylo, and R. E. Huie, J. of Geophys. Res., 96, 13.009-13.015 (1991).

A. Title of Research Task

Determination of Spectroscopic Properties of Atmospheric Molecules from High Resolution Vacuum Ultraviolet Cross Section and Wavelength Measurements

B. Investigators and Institutions

Principal Investigator: W. H. Parkinson

Co-Investigators: K. Yoshino  
D. E. Freeman

Institution: Smithsonian Institution  
Smithsonian Astrophysical Observatory

C. Abstract of Research Objectives

In the wavelength region 185-200 nm, the penetration of solar radiation into the Earth's atmosphere is controlled by photoabsorption of  $O_2$  and  $O_3$ . The transmitted radiation is available to dissociate trace species such as  $N_2O$  and chlorofluorocarbon. The Schumann-Runge absorption bands of  $O_2$  and their extensive predissociation are of considerable atmospheric significance in connection with the transmission of solar radiation and the product of  $O(^3P)$  atoms. The cross sections of the Schumann-Runge bands consist of hundreds of broadened and often overlapping rovibronic lines. The predissociation of  $O_2$  is the main source of odd oxygen in the atmosphere above 60 km. The cross sections are also temperature dependent and can only be obtained from a set of parameters which include predissociation line widths, band oscillator strengths, and line center positions.

D. Summary of Progress and Results

The predissociation of the oxygen molecule in the Schumann-Runge bands is of particular importance in atmospheric chemistry. The Schumann-Runge absorption bands are extensively predissociated, so that the absorption cross section is essentially the cross section for the production of atomic oxygen. This cross section consists of hundreds of broadened and overlapping lines. They may vary by two orders of magnitude between peaks and valleys of a given vibronic band, so that details of the rovibronic linewidths determine the depth to which solar radiation may penetrate into the atmosphere. From our absorption cross sections measurements of the (1,0)–(12,0) bands of  $^{16}O_2$ , 395 predissociation linewidths were obtained, 114 predissociation linewidths of  $^{18}O_2$  and 186  $^{16}O^{18}O$  from the (3,0)–(11,0) bands. The results are published in the Journal of Chemical Physics (Cheung *et al.*, 1990; Chiu *et al.*, 1990).

High resolution absorption cross section measurements in the transmission window regions of the Schumann-Runge bands of oxygen have also been completed. The pressure dependent part of cross sections are subtracted from the observed cross sections to obtain the cross sections at zero pressure. After averaging all observed



measurements made with different pressure, the cross section in the transmission windows are obtained for (2, 0)–(12, 0) bands in wavelength region 179.2–198.2 nm. The cross sections of the Schumann-Runge bands are obtained from the combination of the window cross sections and the peak cross sections previously obtained (Yoshino *et al.*, 1983).

Below the 205 nm region, the observed cross sections are a combination of the Schumann-Runge bands, the Herzberg continuum, cross sections involving two molecules, and Rayleigh scattering. We have obtained the molecular constants of the upper state,  $B^3\Sigma_u^-$ , of the Schumann-Runge system (Cheung *et al.*, 1986), the band oscillator strengths of the Schumann-Runge bands (Yoshino *et al.*, 1988), and the predissociation linewidths as mentioned above. Therefore, we can calculate cross sections of the Schumann-Runge bands at any temperature with Hönl–London factors together with the Boltzmann population factors. Differences between the calculated and observed cross sections at the transmission windows are the cross section,  $\sigma_0$ , including the Herzberg continuum,  $\sigma_H$ , and Rayleigh scattering  $\sigma_R$  cross sections. The Herzberg continuum cross sections obtained are significantly smaller than any previous measurements.

#### References:

- Cheung, A. S.-C., Yoshino, K., Parkinson, W. H., and Freeman, D. E. 1986, *Molecular Spectroscopic Constants of  $O_2$  ( $^3\Sigma_u^-$ )*, J. Mol. Spectrosc. **119**, 1.
- Yoshino, K., Freeman, D. E., Esmond, J. R., Friedman, R. S., and Parkinson, W. H. 1988, *High Resolution Absorption Cross Sections and Band Oscillator Strengths of the Schumann-Runge Absorption Bands of Isotopic Oxygen,  $O_2$  at 79 K*, Planet. Space Sci. **36**, 1201.
- Yoshino, K., Freeman, D. E., Esmond, J. R., and Parkinson, W. H. 1983, *High Resolution Absorption Cross Sections Measurements and Band Oscillator Strengths of the (1,0) - (12-0) Schumann-Runge Bands of  $O_2$* , Planet. Space Sci. **31**, 339.

#### E. Journal Publications

- Predissociation Line Widths of the (1,0)-(12,0) Schumann-Runge Absorption Bands of  $O_2$  in the Wavelength Region 179-202 nm, A.S-C. Cheung, K. Yoshino, J.R. Esmond, S.S-L. Chiu, D.E. Freeman and W.H. Parkinson, *J. Chem. Phys.* **92**, 842-849 (1990).
- Predissociation Line Widths of the (3,0)-(11,0) Schumann-Runge Absorption Bands of  $^{18}O_2$  and  $^{16}O^{18}O$  in the Wavelength Region 180-196 nm, S.S-L. Chiu, A.S-C. Cheung, K. Yoshino, J.R. Esmond, D.E. Freeman and W.H. Parkinson, *J. Chem. Phys.* **93**, 5539-5543 (1990).
- On the Formation of Ozone by Irradiation of Oxygen at 248 Nanometers, D.E. Freeman, K. Yoshino, and W.H. Parkinson, *Science*, **250**, 1432-1433 (1990).
- High Resolution Absorption Cross Sections in the Transmission Window Region of the Schumann-Runge Bands and Herzberg continuum of  $O_2$ , K. Yoshino, J.R. Esmond, A.S-C. Cheung, D.E. Freeman and W.H. Parkinson, *Planet. Space Sci.* accepted for publication, 1991.

Electronic Spectroscopy of HO<sub>2</sub> Radicals  
NASA Research Grant NAGW-1670  
James P. Reilly, Dept. of Chemistry, Indiana University

Objectives

The goal of this work was to clarify the assignment of an electronic absorption spectrum previously believed to be associated with HO<sub>2</sub> radicals. Rotational structure recorded under high resolution conditions was interpreted in order to conclusively identify the species involved.

Results

In the fall of 1987 during a photoacoustic study of hydrogen peroxide's fourth vibrational overtone band we observed a remarkably clear and well resolved spectrum. Its periodicity and K subband structure suggested that the spectrum was not of hydrogen peroxide but of a smaller near-prolate symmetric top molecule. Furthermore, the time dependant behavior of the signal indicated that chemical changes were taking place within the photoacoustic apparatus.

A molecule that contains only hydrogen and oxygen and has roughly appropriate rotational constants to match the observed spectrum is the OOH radical. Its ground state rotational constants are as follows:

$$A''=20.35656 \text{ cm}^{-1} \quad B''=1.117901 \text{ cm}^{-1} \quad C''=1.05643 \text{ cm}^{-1}$$

The radical's large A constant leads one to expect large spacings between K subbands. OOH's relatively small and approximately equal B and C rotational constants should lead to small spacings within K subbands. Qualitatively, these expectations matched the observed patterns and we tentatively identified the molecule as OOH.

Rotational simulations were then conducted using the literature ground state rotational constants for the OOH radical. Fine tuning of the upper state rotational constants was accomplished with a simplex least squares optimization program using the assignments and wavelength information from the experimental spectrum. While the overall position of the K subbands was in good agreement with experiment, the line spacings and band head positions within the subbands did not match exactly. A more detailed, high resolution experimental spectrum was necessary before the ambiguity within the K subbands could be resolved.

We recorded high resolution, individual K subband spectra with a Spectra Physics 380D ring dye laser operating single mode with the photoacoustic cell positioned within the laser cavity. A complete spectrum was generated by adding together many smaller overlapping scans each typically 1 cm<sup>-1</sup> in length. The signal intensity was found to diminish for the five R branches at long wavelengths. This was in part due to chemistry within the photoacoustic cell reducing the population of the radicals. Fewer rotational lines were observed for higher subbands since J ≥ K. After 5-6 hours all traces of the spectrum disappeared and a hydrogen peroxide spectrum could then be recorded.

Comparison of high resolution experimental spectra and simulations indicated a serious discrepancy. The spacings within and between P, Q and R branches were clearly not correct. In order to fine tune the upper state rotational constants another simplex least squares optimization was conducted using the more precise high resolution spectral data. Under these conditions the program could not match the data to within its experimental accuracy.

Further manipulation of the simulation's rotational constants provided a clue as to the problem. Much better agreement between experiment and simulation could be obtained by varying both the upper and lower state rotational constants. Since this was the case it was no longer clear that OOH was responsible for the spectrum that we have been observing.

Our experimental procedure for producing the unknown spectrum was re-evaluated. In order to generate the spectrum it was necessary to completely disassemble, clean and reassemble the photoacoustic apparatus. A photoacoustic cell design that contained o-rings instead of epoxy failed to produce the desired spectrum unless it was first exposed to the epoxy. Mass spectroscopic analysis of the epoxy outgassing products indicated the presence of diethylenetriamine, a primary/secondary amine known to react with peroxides. By introducing pure diethylenetriamine into o-ringed photoacoustic cells that had yielded no data, beautiful spectra were immediately generated.

It was now clear that more elements than just hydrogen and oxygen were present in the photoacoustic apparatus and that the range of possible species capable of producing the rotationally resolved spectrum would have to be expanded. The OOH radical did have a geometry close to what was necessary but increases to both the B and C rotational parameters were found to improve the experimental/simulation agreement. An increase in the B and C rotational constants results from replacing one of the oxygen atoms in OOH with an atom of lower mass. This has the effect of reducing the moment of inertia about the B and C rotational axis and increasing the rotational constants. The A rotational constant is largely unaffected by this change as the mass change is virtually along the A rotational axis.

Of the possible hydrogen, nitrogen, carbon and oxygen arrangements, the molecule HNO became a prime suspect. Rotational constants for HNO have been previously obtained by flash photolysis, microwave spectroscopy, and microwave/visible double resonance methods. These rotational constants are as follows:

$$\begin{array}{lll} A' = 21.95460 \text{ cm}^{-1} & B' = 1.325500 \text{ cm}^{-1} & C' = 1.242600 \text{ cm}^{-1} \\ A'' = 18.46343 \text{ cm}^{-1} & B'' = 1.410284 \text{ cm}^{-1} & C'' = 1.305649 \text{ cm}^{-1}. \end{array}$$

These values were then used to perform another rotational simulation. The simulation's line spacings were found to be in good agreement with experiment for subbands near the origin. (Other simulated subbands were also in good agreement but they suffer from K-dependant rotational perturbations.) HNO is known to have an electronic  $A^1A'' \rightarrow X^1A'$  transition occurring at 760.2 nm. This wavelength compares well with our estimated transition origin of 760 nm. We therefore conclude that we have been recording  $A^1A'' \rightarrow X^1A'$  (0,0) spectra of HNO produced by the reaction of  $H_2O_2$  with diethylenetriamine, a component of torr-seal epoxy.

Superb spectra of this transition have already been recorded by Dalby [Can. J. Phys. 36, 1336 (1958)] and Ramsay [Can. J. Phys. 40, 322 (1962)]. Because of this, work on this project was discontinued.

#### A. Title of Research Task

Laboratory Spectroscopic Measurements Relevant to Upper Atmospheric Research. (Grant-in-Aid No. NAGW-1238).

#### B. Investigator and Institution

Prasad Varanasi, Professor of Atmospheric Sciences, Institute for Terrestrial and Planetary Atmospheres, State University of New York, Stony Brook, NY 11794-2300.

#### C. Abstract of Research Objectives

Absolute intensities, air-broadened half-widths, and pressure-induced shifts of infrared spectral lines of atmospheric trace gases are measured. The laboratory measurements, conceived after consultations with the principal investigators of NASA's UARS and ATMOS missions, yield data which are valuable in the interpretation of many of the remote sensing experiments conducted by NASA in the atmosphere. Our data are obtained at temperature-pressure combinations that represent tangent heights (in ATMOS type solar-occultation experiments) or layers in the atmosphere using cryogenically cooled absorption cells and the Doppler-limited spectral resolution ( $\sim 10^{-4} \text{ cm}^{-1}$ ) of a tunable diode laser spectrometer.

#### D. Summary of Progress and Results

We have measured spectral absorption coefficients, which are also known as absorption cross-sections,  $k_\nu$  ( $\text{cm}^{-1} \text{ atm}^{-1}$ ), of HCFC-22 around  $829.0 \text{ cm}^{-1}$ , and of CFC-12 around  $921.7 \text{ cm}^{-1}$ ,  $923 \text{ cm}^{-1}$ , and  $1106 \text{ cm}^{-1}$ . The  $k_\nu$  data measured employing the tunable diode laser spectrometer are free of instrumental distortion and are more practical in these cases than hundreds of spectral line parameters adapted in conventional line-by-line procedures. The present set of data obtained with  $\text{N}_2$  as the broadening gas are shown to be directly applicable to real atmospheric observations as, for example, the spectra recorded by the ATMOS/Spacelab 3 interferometer.

The absolute intensities and collision-broadened half-widths of several lines in the  $\nu_5$ -fundamental bands of  $^{12}\text{C}_2\text{H}_2$  and  $^{12}\text{C}^{13}\text{CH}_2$  have been measured at various temperatures between 147 and 295 K. The temperature dependence of the collision-broadened half-width has been determined for lines broadened by Ar and  $\text{N}_2$ . Self-broadened linewidths of  $^{12}\text{C}_2\text{H}_2$  and  $^{12}\text{C}^{13}\text{CH}_2$  have also been retrieved from our measurements. From the measured line intensities we have obtained  $S_\nu = 588 \text{ cm}^{-2} \text{ atm}^{-1}$  for the absolute intensity of the  $\nu_5$ -fundamental of  $^{12}\text{C}_2\text{H}_2$  at 294 K. The band intensity determined by Varanasi et al<sup>1</sup> was 596 at 296 K which was used to generate an atlas that was later incorporated into the GEISA spectroscopic line parameters data bank.<sup>2</sup> It would seem now that that atlas has

<sup>1</sup>P. Varanasi et al, *JQSRT* **30**, 497 (1983).

<sup>2</sup>N. Husson et al, *Annales Geophysicae* **4**, 185 (1986).

been reliable within 2% error as far as the  $\nu_5$ -fundamental of  $^{12}\text{C}_2\text{H}_2$  is concerned. The remarkable agreement if not coincidence within the stated experimental errors between the measured line intensities and those computed using the highly simplified formulation of Varanasi et al<sup>1</sup> would clearly suggest that the so-called Herman-Wallis factors are practically unity. The band strengths of  $^{12}\text{C}_2\text{H}_2$  and  $^{12}\text{C}^{13}\text{CH}_2$  differ by only  $1.050 \pm 0.024$ , which means that, within the experimental error bounds of the data for each isotope, the vibrational transition moments are the same. *Our data on the temperature dependence of directly measured linewidths of  $^{12}\text{C}_2\text{H}_2$  and on linewidths and intensities of  $^{12}\text{C}^{13}\text{CH}_2$  are, to the best of our knowledge, the first ever reported.* We also believe the intensity data to be the most accurate and extensive on  $\nu_5$ -fundamental bands.

The absolute intensity and collision-broadened half-widths of the  $5_{0,5} \rightarrow 5_{1,5}$  transition at  $951.7393 \text{ cm}^{-1}$  in the  $\nu_7$ -fundamental band of  $^{12}\text{C}_2\text{H}_4$  have been measured at 202, 252 and 295 K with our diode laser spectrometer. The temperature dependence of the half-width has been determined for the cases of the line broadened by  $\text{N}_2$ . This line is one of the  $^{12}\text{C}_2\text{H}_4$  lines often used in the calibration of photoacoustic measurements using the  $10 \mu\text{m}$   $\text{CO}_2$  laser. *There appear to be no other data available at the present time for direct comparison with our results.*

We have also examined a few lines in the  $\nu_2$ -fundamental bands of the  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  in the  $10 \mu\text{m}$  region as some of these lines appear in the atmospheric spectra of molecules which are more actively studied in remote sensing. *It would seem that these are the first of their kind measurements of Ar-, and  $\text{N}_2$ - broadened line widths at low temperatures.* A manuscript summarizing some of these measurements is under preparation for publication in *JQSRT*.

#### E. Journal Publications

P. Varanasi: "Intensity and Line Width Measurements in the  $13.7 \mu\text{m}$  Fundamental Bands of  $^{12}\text{C}_2\text{H}_2$   $^{12}\text{C}^{13}\text{CH}_2$  at Planetary Atmospheric Temperatures." *JQSRT* (in press).

J. F. Brannon Jr. and P. Varanasi, "Tunable Diode Laser Measurements on the  $951.7393 \text{ cm}^{-1}$  Line of  $^{12}\text{C}_2\text{H}_4$  at Planetary Atmospheric Temperatures." *JQSRT* (in press).

P. Varanasi, "Absorption Coefficients of HCFC-22 around  $829 \text{ cm}^{-1}$  at Atmospheric Conditions." *JQSRT* (in press).

P. Varanasi, "Absorption Cross-sections of CFC-12 Relevant to Atmospheric Remote Sensing." *JQSRT* (in press).

P. Varanasi, "Line Intensities, Collision-broadened Line Widths and Pressure-induced Line Shifts in the  $\nu_2$ -fundamentals of  $\text{NH}_3$  at Low Temperatures." (Manuscript under preparation for submission to *JQSRT*).

## **A. INFRARED LABORATORY SPECTROSCOPY IN SUPPORT OF STRATOSPHERIC MEASUREMENTS**

### **INFRARED LABORATORY SPECTROSCOPY IN SUPPORT OF ATMOS**

**B. Principal investigator:** Robert A. Toth

**Co-Investigator:** Linda R. Brown

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## **C. ABSTRACT OF RESEARCH OBJECTIVES**

The objective of this program is the acquisition and analysis of molecular spectral parameters for the 2 to 16  $\mu\text{m}$  region in order that data obtained from stratospheric measurements programs can be properly interpreted. Field instruments such as the Atmos and Mark IV interferometers have spectral resolutions of  $0.01\text{ cm}^{-1}$  and  $0.005\text{ cm}^{-1}$ , respectively, which require that laboratory measurements, which support these efforts, be obtained at comparable or better spectral resolutions.

For this program, conventional spectroscopic techniques are used to analyze infrared spectra obtained in the laboratory. Spectra are recorded at  $0.0028$ ,  $0.005$  and  $0.01\text{ cm}^{-1}$  resolutions using an interferometer located in the McMath facility at the Kitt Peak National Observatory. The gases studied include the normal trace species such as  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  and less abundant trace gases such as  $\text{H}_2\text{CO}$ ,  $\text{NO}_2$ ,  $\text{COF}_2$ , and  $\text{CH}_3\text{Cl}$ . The molecules of the first category produce absorptions over wide expanses of the stratospheric spectrum which, in many cases, overlap or blend with spectral features of the less abundant species. Therefore, in order to obtain an accurate estimate of the stratospheric concentration of the less abundant gases using infrared techniques requires not only an accurate estimate of the line parameters of these species but also a detailed knowledge of the line parameters of the normal trace gases.

## **D. SUMMARY OF PROGRESS AND RESULTS**

Our efforts have been focused on compiling accurate spectral parameters derived from laboratory measurements for use in the reduction of stratospheric data. A large portion of this compilation has already been used in the various analysis of ATMOS spectra obtained from Spacelab 3. Listings of spectral parameters derived from our laboratory measurements which are presently available to ATMOS investigators include the following:  $\text{N}_2\text{O}$  ( $500\text{--}4100\text{ cm}^{-1}$ ),  $\text{CH}_4$  ( $1100\text{--}4700\text{ cm}^{-1}$ ),  $\text{NO}_2$  ( $1520\text{--}1660\text{ cm}^{-1}$ ),  $\text{HDO}$  ( $1000\text{--}4400\text{ cm}^{-1}$ ),  $\text{CO}_2$  ( $1200\text{--}1400\text{ cm}^{-1}$ ), and  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ , and  $\text{H}_2^{18}\text{O}$  ( $900\text{--}4400\text{ cm}^{-1}$ ).

During 1990 and 1991, the line positions and strengths of  $\text{NO}_2$  in the  $6.2\text{ }\mu\text{m}$  region were measured and fully analyzed for transitions in the very strong  $\nu_3$  band and the hot band;  $\nu_2+\nu_3-\nu_2$ . Measurements of line positions and strengths of the  $\nu_2$  bands of  $\text{H}_2^{17}\text{O}$  and  $\text{H}_2^{18}\text{O}$  were analyzed using the quantum mechanical model developed for the  $\nu_2$  band of  $\text{H}_2^{16}\text{O}$  (see reference 2). Spectra of  $\text{OCS}$  and  $\text{N}_2\text{O}$

were obtained with a Fourier transform spectrometer located at the Kitt Peak National Observatory and these data will be used to determine calibration frequency standards for the  $2.4\ \mu\text{m}$  spectral region. Theoretical modelling of the three interacting bands of  $\text{H}_2\text{O}$ , whose transitions are observed between  $2700$  and  $4500\ \text{cm}^{-1}$ , was begun. Measurements and observed values of line positions and strengths of  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{17}\text{O}$  and  $\text{H}_2^{18}\text{O}$  in this spectral region have been obtained from data recorded at the Kitt Peak facility. New measurements and observed values of line positions and strengths of methane have been obtained for the  $2200$  to  $3300\ \text{cm}^{-1}$  region and the analysis of the five interacting  $\text{CH}_4$  bands will continue.

#### E. PUBLICATIONS

1. C. P. Rinsland, M. R. Gunson, J. C. Foster, R. A. Toth, C. B. Farmer, and R. Zander, "Stratospheric profiles of heavy water vapor isotopes and  $\text{CH}_3\text{D}$  from analysis of the ATMOS Spacelab 3 infrared solar spectra," J. Geophys. Res. 96, 1057-1068 (1991).
2. R. A. Toth, "The  $\nu_2$  band of  $\text{H}_2^{16}\text{O}$  - line strengths and transition frequencies," J. Opt. Soc. Am. B (in press).
3. R. A. Toth, "Line frequency measurements and analysis of  $\text{N}_2\text{O}$  between  $900$  and  $4700\ \text{cm}^{-1}$ ," Appl. Opt. (in press).
4. R. A. Toth, "High resolution measurements and analysis of  $\text{NO}_2$  in the  $(001)-(000)$  and  $(011)-(010)$  bands," J. Opt. Soc. Am. B (submitted for publication).
5. N. Lacome, L. R. Brown and C. Chackerian, Jr., "Collisional line mixing with the  $^R\text{Q}_0$  branch of the  $\nu_5$  band of  $\text{CH}_3\text{Cl}$ ," The 46th Symposium on Molecular Spectroscopy, Abstract WF1, The Ohio State University (1991).

## **High Resolution Spectroscopy to Support Atmospheric Measurements**

### **Investigators and Institutions**

P.I.: Dr. Mary Ann H. Smith, NASA Langley Research Center  
Co-I's: Dr. V. Malathy Devi, College of William and Mary  
Dr. Curtis P. Rinsland, NASA Langley Research Center  
Dr. D. Chris Benner, College of William and Mary

### **Abstract of Research Objectives**

Detailed knowledge of the molecular spectra of ozone and other infrared-active atmospheric species is needed for accurate calculation of atmospheric heating and cooling rates in climate models. Remote sensing experiments on the Nimbus-7 satellite and the Spacelab-3 shuttle mission have shown that space-based measurements of infrared absorption or emission can be used to accurately determine the concentrations and distributions of stratospheric species on a global scale. The objective of this research task is to improve knowledge of the spectroscopic line parameters (positions, intensities, assignments, halfwidths, and pressure-induced shifts) of key atmospheric constituents through laboratory measurements.

### **Summary of Progress and Results**

In 1990 and 1991 we have recorded new high-quality spectra of pure ozone and ozone-air mixtures at a series of temperatures from room temperature down to  $-63^{\circ}\text{C}$ . These measurements utilized the McMath high-resolution Fourier Transform Spectrometer (FTS) at the National Solar Observatory on Kitt Peak, Arizona, and a coolable absorption cell designed and built at NASA Langley Research Center. The spectra cover several absorption bands in the 4 to  $15\text{ }\mu\text{m}$  region, and are being analyzed to determine the behavior of pressure broadening and shift coefficients at low temperatures typical of those found in the upper atmosphere. Spectra of mixtures of  $\text{H}_2\text{O}$ , HDO, and  $\text{D}_2\text{O}$  in air,  $\text{N}_2$ , or  $\text{O}_2$  at room temperature were also recorded in 1990; analyses of broadening and shifts of HDO and  $\text{D}_2\text{O}$  lines in these spectra have been completed.

Continuing analysis of room-temperature ozone absorption spectra recorded by us in 1984, 1985, 1987, and 1989 has resulted in improved line positions, intensities, and assignments in the 2.5 to  $15\text{ }\mu\text{m}$  region. Data analysis is performed primarily at Langley Research Center, and the theoretical interpretation of the results is being done in collaboration with investigators at several other institutions in the United States and France. Recent results include analyses of absorption bands of the  $^{17}\text{O}$ - and  $^{18}\text{O}$ -enhanced isotopic ozone species which had not previously been measured. Analysis of self-broadening coefficients for 355 lines belonging to 5 different bands in the 5 to  $15\text{ }\mu\text{m}$  region has been completed, and determination of  $\text{N}_2$ -,  $\text{O}_2$ -, and air-broadening coefficients and pressure-induced line shifts in the  $3\text{ }\mu\text{m}$  region is nearly complete.



We have also continued our analyses of previously recorded room-temperature spectra of methane and two of its isotopic variants in mixtures with N<sub>2</sub>, O<sub>2</sub>, Ar, or air to determine broadening coefficients and pressure-induced line shifts for a large number of absorption lines belonging to several different vibration-rotation bands. We have most recently completed analysis of O<sub>2</sub>-broadening and shifts in the 3  $\mu\text{m}$  and 2.5  $\mu\text{m}$  bands and have compared these results to those previously obtained by us for N<sub>2</sub>- and air-broadening. In 1989 we recorded a series of spectra of methane broadened by air and by N<sub>2</sub> over the same temperature range as the 1990-1991 ozone spectra; analysis of these spectra to determine the temperature-dependence of the broadening and shift coefficients has been completed and will be submitted for publication in the near future.

### Journal Publications

C. Camy-Peyret, J.-M. Flaud, C.P. Rinsland, M.A.H. Smith, V. Malathy Devi, and A. Goldman: Line parameters for ozone hot bands in the 4.8- $\mu\text{m}$  spectral region. J. Mol. Spectrosc. **139**, 353-360 (1990).

C. Camy-Peyret, J.-M. Flaud, M.A.H. Smith, C.P. Rinsland, V. Malathy Devi, J.J. Plateaux, and A. Barbe: The 3.3- $\mu\text{m}$  bands of ozone: Line positions and intensities. J. Mol. Spectrosc. **141**, 134-144 (1990).

J.-M. Flaud, C. Camy-Peyret, C.P. Rinsland, V. Malathy Devi, M.A.H. Smith, and A. Goldman: Improved line parameters for ozone bands in the 10- $\mu\text{m}$  spectral region. Appl. Opt. **29**, 3667-3671 (1990).

J.-M. Flaud, C. Camy-Peyret, C.P. Rinsland, M.A.H. Smith, and V. Malathy Devi: Atlas of ozone spectral parameters from microwave to medium infrared. Academic Press, Cambridge, Massachusetts (1990).

V. Malathy Devi, A. Perrin, J.-M. Flaud, C. Camy-Peyret, C.P. Rinsland, and M.A.H. Smith: Line positions and intensities for the  $\nu_2 + 3\nu_3$  band of <sup>16</sup>O<sub>3</sub> around 2.7  $\mu\text{m}$ . J. Mol. Spectrosc. **143**, 381-388 (1990).

A. Perrin, A.-M. Vasserot, J.-M. Flaud, C. Camy-Peyret, C.P. Rinsland, M.A.H. Smith, and V. Malathy Devi: The  $\nu_2$  bands of <sup>18</sup>O<sub>3</sub>, <sup>18</sup>O<sup>16</sup>O<sup>18</sup>O, and <sup>16</sup>O<sup>18</sup>O<sup>18</sup>O: Line positions and intensities. J. Mol. Spectrosc. **143**, 311-317 (1990).

C.P. Rinsland, M.A.H. Smith, V. Malathy Devi, J.-M. Flaud, and C. Camy-Peyret: The  $2\nu_2 + \nu_3$  and  $2\nu_2 + \nu_1$  bands of <sup>16</sup>O<sub>3</sub> at 4.1  $\mu\text{m}$ : Line positions and intensities. J. Mol. Spectrosc. **139**, 343-352 (1990).

A. Perrin, A.-M. Vasserot, J.-M. Flaud, C. Camy-Peyret, V. Malathy Devi, M.A.H. Smith, C.P. Rinsland, A. Barbe, S. Bouazza, and J.J. Plateaux: The 2.5  $\mu\text{m}$  bands of ozone: Line positions and intensities. J. Mol. Spectrosc., in press (1991).

C.P. Rinsland, M.A.H. Smith, V. Malathy Devi, A. Perrin, J.-M. Flaud, and C. Camy-Peyret: The  $\nu_2$  bands of  $^{16}\text{O}^{17}\text{O}^{16}\text{O}$  and  $^{16}\text{O}^{16}\text{O}^{17}\text{O}$ : Line positions and intensities. J. Mol. Spectrosc., in press (1991).

C.P. Rinsland, M.A.H. Smith, V. Malathy Devi, and D.C. Benner: Measurements of Lorentz-broadening coefficients and pressure-induced line shift coefficients in the  $\nu_2$  band of  $\text{D}_2^{16}\text{O}$ . J. Mol. Spectrosc., in press (1991).

C.P. Rinsland, M.A.H. Smith, V. Malathy Devi, and D.C. Benner: Measurements of Lorentz-broadening coefficients and pressure-induced line shift coefficients in the  $\nu_2$  band of  $\text{HD}^{16}\text{O}$ . Manuscript submitted to J. Mol. Spectrosc. (1991).

C.P. Rinsland, A. Goldman, M.A.H. Smith, and V. Malathy Devi: Measurements of Lorentz air-broadening coefficients and relative intensities in the  $\text{H}_2^{16}\text{O}$  pure rotational and  $\nu_2$  bands from long horizontal path atmospheric spectra. Appl. Opt. **30**, 1427-1437 (1991).

M.A.H. Smith, C.P. Rinsland, V. Malathy Devi, L.S. Rothman, and K. Narahari Rao: Intensities and collision broadening parameters from infrared spectra: An update. In Spectroscopy of the Earth's Atmosphere and Interstellar Molecules, edited by K. Narahari Rao and A. Weber. Academic Press, Cambridge, Massachusetts, in press (1991).

M.A.H. Smith, C.P. Rinsland, and V. Malathy Devi: Measurements of self-broadening of infrared absorption lines of ozone. J. Mol. Spectrosc. **147**, 142-154 (1991).

## Collision Induced IR Absorptions in Oxygen and Nitrogen

### Principal Investigators:

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### Research Objectives:

The background continuum absorption in the atmosphere due to collision-induced effects between colliding pairs of non-polar molecules such as  $N_2-N_2$ ,  $O_2-O_2$ , and  $O_2-N_2$  appears to set an upper limit to the present accuracy with which the absorption due to a number of minor molecular species can be determined. Although this continuum absorption is quite weak, over a long path through the atmosphere, its effects can be significant. One of the goals of this project is to measure accurately this absorption in the temperature range 190-300K. Another objective of this research is to study the high resolution IR spectra of a number of molecular species which play a role in stratospheric chemistry. The particular interest of this work is to examine the spectrum of chlorine containing species such as  $OCIO$  and  $HOCl$  and to obtain and analyze the spectrum of the fundamental bands of formic acid ( $HCOOH$ ).

### Summary of Progress:

Collision-Induced Absorption: The construction of a multiple pass White absorption cell (designed by W. B. Olson) for the measurement of this weak effect is almost completed and should be finished by October 1991. This cell has a base path length of 2 meters and has a maximum optical path length of 116 meters (58 transversals). Collision-induced absorption is proportional to the square of the pressure and, in order to obtain accurate intensity measurements, it will be necessary to take these measurements at high pressures. The cell is designed to operate up to 20 atm pressure and be coolable to ( $-80^\circ C$ ). To maintain the integrity of the optical alignment over a wide range of temperature the mirrors are made of zerodur and the mirror assembly is mounted on a frame of four super-invar rods. Adjustment of the optical path length can be accomplished while the cell is under vacuum, or pressure, and at low temperature. In order to avoid problems of contamination, the cell is constructed of stainless steel. The absorption cell will be interfaced to a BOMEM FTS spectrometer. A transfer optics system coupling the cell with the spectrometer has been constructed. The optical path between the spectrometer and the absorption cell is fully evacuated to avoid any absorptions due to ambient air.

High Resolution Infrared Studies: An extensive study of a number of bands of  $\text{OClO}$  is well underway. The spectra of all three fundamental bands as well as the  $2\nu_1$  and  $\nu_1+\nu_3$  bands of  $\text{OClO}$  have been obtained by C.J. Howard and J.B. Burkholder at the NOAA laboratories in Boulder. This molecule is one of the few stable molecules with an odd number of electrons, and the resulting spin splitting complicates the spectrum considerably since each line is doubled. The molecule is a fairly asymmetric near prolate rotor with  $\kappa \approx -0.92$ , and expansion techniques which were used in this laboratory to account for the spin splitting in the  $\text{NO}_2$  molecule were found to be inadequate to treat the observed spin splitting in this molecule. In collaboration with J. Ortigoso and R. Escribano at CSIC in Madrid, a program has been written to calculate the energy levels exactly. This program uses a standard Watson rotational Hamiltonian in A-reduced form. A Van Vleck spin-rotation Hamiltonian was used. The expressions of Brown and Sears were also incorporated into the program to account for the large centrifugal distortion effects observed for the spin splitting. The analysis of the  $\nu_1$  and  $\nu_2$  b-type fundamental bands at  $946\text{ cm}^{-1}$  and  $448\text{ cm}^{-1}$  respectively and the a-type fundamental band,  $\nu_3$ , at  $1110\text{ cm}^{-1}$  of both the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  isotopic species has been completed. A "hot band",  $\nu_1+\nu_2-\nu_2$ , has also been assigned. Ground state combination differences from these bands have been combined with all available ground state microwave data to obtain a refined set of ground state rotational and spin splitting constants. Upper state constants of the bands have also been obtained by fitting both the observed IR data and the available microwave data. With the spectroscopic constants obtained from the fitting, the line spectra of each band can be predicted with an accuracy of better than  $\pm 0.001\text{ cm}^{-1}$  over the quantum number range  $N=0$  through 40 and  $K_a \leq 17$ . The strongest lines in the b-type bands are the  $^1R_0$ ,  $^1P_0$ ,  $^3R_1$ , and  $^3P_1$  series where the spin splitting is unresolved. These lines should be ideal candidates for use in remote sensing of  $\text{OClO}$ . Work on the  $2\nu_1$  band at  $1890\text{ cm}^{-1}$  and the  $\nu_1+\nu_3$  band at  $1950\text{ cm}^{-1}$  is almost completed. In addition to  $\text{OClO}$ , we are working on the line assignment of the  $\nu_1$  band of the  $\text{HOCl}$  molecule. These spectra were also obtained by Burkholder and Howard at NOAA. This band is a beautiful type-a type-b hybrid band and has been studied at much lower resolution and wavenumber precision previously in this laboratory. With this new data, a significantly improved set of not only upper state but ground state spectroscopic constants as well will be obtained.

Publication:

"High Resolution Infrared Spectrum of the  $\nu_1$  Band of  $\text{OClO}$ ", J. Ortigoso, R. Escribano, J.B. Burkholder, C.J. Howard and W.J. Lafferty, *J. Mol. Spectrosc.* 148, 346(1991).

## Research Summary 1990-1991

### A. Title of Research.

Atomic and Molecular Frequency Calibration Standards and Tunable Laser Spectroscopy in Support of Upper Atmospheric Research.

### B. Investigators and Institutions.

NIST Time and Frequency Division (full time employees and contractors):

Dr. J. S. Wells and Dr. Leo Hollberg, co-Principal Investigators

Dr. D. A. Jennings, Dr. A. G. Maki, M. D. Vanek, R. Fox, and N. Mackie

NIST Time and Frequency Division guest workers contributing to the work cited: Dr. M. Schneider, Institut für Angewandte Physik, Uni-Bonn, Bonn, FRG

Drs. A. S. Zibrov and V.L. Velichansky, Lebedev Phys. Inst., Moscow, USSR

Dr. R. Ellingsen, Norwegian Inst. of Tech., Trondheim, Norway

Dr. H. G. Robinson, Dept. of Physics, Duke Univ., Durham, N. C.

### C. Abstract of Research Objectives.

The primary objective of this research has been to provide reference tables (in the 0 to 3000  $\text{cm}^{-1}$  region) of frequencies of molecular transitions along with other information such as relative intensities and lower energy levels. The program has been recently expanded to include atomic transitions. These values serve as frequency or wavenumber calibration points, not only for spectroscopic studies of molecules and atoms in the upper atmosphere, but also for the community of spectroscopists at large. The first step in the generation of these tables requires accurate heterodyne frequency measurements which are traceable to  $\text{CO}_2$  laser standards (often through the use of a CO laser transfer oscillator). A second step in the generation of the reference tables involves fitting the data and predicting values for calibration tables from the newly determined constants.

### D. Summary of Progress and Results.

Extension of CO laser operation [1] to the 2 $\rightarrow$ 1 band and subsequent measurements permitted calculated values for the 1 $\rightarrow$ 0 band from previous measurements on the 2 $\rightarrow$ 0 band. The low  $\nu''$  operation included the bands, 5 $\rightarrow$ 4, 4 $\rightarrow$ 3, 3 $\rightarrow$ 2, and 2 $\rightarrow$ 1. Operation on these bands and simultaneous measurements of their frequencies permitted transfer oscillator type heterodyne frequency measurements [2] on OCS bands at 2060  $\text{cm}^{-1}$  for the first time. Extension to even higher frequencies required the use of  $\text{CO}_2$  laser radiation which had its frequency doubled in a solid state crystal at 77 K. A limited number (TDL limitation) of new [3] frequency measurements were made on both OCS and CO in the 2100  $\text{cm}^{-1}$  region.

Hot bands were used to calibrate FTS spectra on OCS in the 2510 to 3150  $\text{cm}^{-1}$  [4]. The CO overtone laser was used for the first time as a transfer oscillator to make direct frequency measurements at the IAP (Institut für Angewandte Physik) on some of these same bands at 87 THz. Additional TDLs will have to be acquired however to complete this joint NIST/IAP effort.

A new approach was devised to measure the pressure induced frequency shift on OCS. This involved a computer controlled frequency offset locked diode laser. Measured shifts [5] were the order of 0.37 kHz/Pa (50 kHz/Torr). This scheme has the potential for greatly enhanced frequency measurements, and is probably second only to sub-Doppler type frequency measurements. The heterodyne apparatus and technique for this control were taken to Bonn and used in an experiment to narrow and control the linewidth of a lead salt laser at 5  $\mu\text{m}$  [6]. By combining the computer controlled

technique with the optical feedback narrowing scheme it will be possible to have a TDL with a linear scan and with a frequency uncertainty and linewidth both of 1 MHz.

Two of the main limitations in using diode lasers for precision spectroscopy are the diode laser's broad spectral linewidths and incomplete spectral coverage due to mode jumps. We have made some progress in combining optical feedback narrowing techniques with grating tuned extended cavity diode lasers in the near infrared. This should allow us to have very narrow linewidths and simultaneously complete spectral coverage.

We have also extended the spectral range of our precision tunable diode laser systems up to the visible region of the spectrum. We now have stabilized the relatively new red diode lasers operating near 660 nm and we have observed saturated absorption signals in calcium on the 657 nm transition [7]. In addition to the red, we have succeeded in generating blue light (near 425 nm) by frequency doubling diode lasers operating near 850 nm. These successes greatly expand our spectroscopic capabilities.

Items [8] and [9] represent the completion of work started earlier.

#### ***E. Journal Publications for 1990 and 1991 (References).***

1. Heterodyne Frequency Measurements of CO Laser Transitions near 2050  $\text{cm}^{-1}$ , M. Schneider, J. S. Wells, and A. G. Maki, *J. Mol. Spectrosc.* **139**, 432-438 (1990).
2. Heterodyne Frequency Measurements of OCS near 61.76 THz (2060  $\text{cm}^{-1}$ ), J. S. Wells, M. Schneider, and A. G. Maki, *J. Mol. Spectrosc.* **140**, 170-176 (1990).
3. Heterodyne Frequency Measurements of CO and OCS Beyond 2100  $\text{cm}^{-1}$ , A. G. Maki, J. S. Wells, and D. A. Jennings, *J. Mol. Spectrosc.* **144**, 224-229 (1990).
4. High Resolution Measurements of the Bands of Carbonyl Sulfide Between 2510 and 3150  $\text{cm}^{-1}$ , A. G. Maki, J. S. Wells, and J. B. Burkholder, *J. Mol. Spectrosc.* **147**, 173-181 (1991).
5. Pressure Dependent Lineshift Measurements on OCS, M. D. Vanek, J. S. Wells, and A. G. Maki, *J. Mol. Spectrosc.* **147**, 398-405 (1991).
- 6.\* Line Narrowing and Control of Lead Salt Lasers by Optical Feedback, M. Mürztz, M. Schaefer, M. Schneider, J. S. Wells, and W. Urban, Intern'l Conference on Monitoring of Gaseous Pollutants by Tunable Diode Lasers, Freiburg, FRG, (Oct. 1991) - Kluwer Academic Press.
7. Diode Lasers and Spectroscopic Applications, L. Hollberg, R. Fox, N. Mackie, A. S. Zibrov, V. L. Velichansky, R. Ellingsen, and H. G. Robinson, Tenth International Conference on Laser Spectroscopy, Font Remeau, France (June 1991) - Springer Verlag.
8. Measurement and Analysis of the Fermi Resonance between  $\nu_5$  and  $2\nu_9$  of Nitric Acid, A. G. Maki and J. S. Wells, *J. Mol. Spectrosc.* (submitted).
9. Calibration Tables From Heterodyne Frequency Measurements, Arthur G. Maki and Joseph S. Wells, NIST Spec. Pub. [est. 700 p.] (1991).

\*Paper [6] describes work at the Institut für Angewandte Physik (in Prof. Urban's group) during the tenure of J. S. Wells appointment as an A. v. Humboldt Senior Scientist Awardee.

**A. LASER LABORATORY SPECTROSCOPY IN SUPPORT OF ATMOSPHERIC MEASUREMENTS**

**B. Principal Investigator:** Dr. Randy D. May  
**Co-Investigator:** Dr. Christopher R. Webster  
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**C. Abstract of Research Objectives**

The laser laboratory spectroscopy program involves the acquisition and analysis of high-resolution molecular spectral data which are required for the interpretation of atmospheric measurements by infrared instruments such as the BLISS and ALIAS diode laser spectrometers, and FTIR instruments such as ATMOS. These data are also required to define the optimum spectral regions to be used for detection of a particular molecular species, to establish the feasibility of new spectroscopic techniques for in-situ and remote sensing of Earth and planetary atmospheres, and to test current theories of molecular lineshape variations with pressure, temperature and gas composition.

**D. Summary of Progress and Results**

Measurements of absolute line intensities in the  $\nu_6$  band of  $\text{H}_2\text{O}_2$  were carried out using an optical arrangement which allowed simultaneous acquisition of both ultraviolet (UV) and infrared (IR) absorption data. With  $\text{H}_2\text{O}_2$  concentrations determined from the UV absorption at 254 nm, where the absorption coefficient for  $\text{H}_2\text{O}_2$  has been measured accurately, linestrengths were extracted from the IR absorption with absolute accuracies of about 7%. The resulting linestrengths were up to 50% larger than previously reported values and, consequently, stratospheric  $\text{H}_2\text{O}_2$  volume mixing ratio upper limits determined from field measurements in the IR are lowered by approximately 50% based on these linestrength values.

Linestrengths, air- and self-broadening parameters have been measured for lines in the  $\nu_4$  ( $1243\text{ cm}^{-1}$ ) and  $\nu_6$  ( $774\text{ cm}^{-1}$ ) bands of carbonyl fluoride ( $\text{COF}_2$ ). These data are required for interpretation of recent observations of  $\text{COF}_2$  features in atmospheric spectra recorded by the ATMOS and Denver University Fourier transform spectrometers. The laboratory

measurements represent the first high-resolution measurements of absolute intensities for these COF<sub>2</sub> bands, and the first measurements of self-broadening in the infrared. Air-broadening parameters were determined at 296 K and at 215 K for use in calculating absorption coefficients at stratospheric temperatures and pressures.

FTIR spectra of HO<sub>2</sub>NO<sub>2</sub> were recorded at high resolution (0.003 cm<sup>-1</sup>) in order to investigate the feasibility of performing a rotational analysis of the strong 803 cm<sup>-1</sup> band which has been observed in ATMOS and Denver University FTIR spectra of the stratosphere. Lower resolution spectra were also recorded at a reduced temperature (250 K) to monitor the profile of the Q-branch as a function of temperature. Diode laser measurements of air-broadening at 240 K and 296 K have also been carried out, as well as low-pressure measurements at 240 K which revealed for the first time clear subband structure in the P- and R-branches of the band. A previously unobserved vibrational band for HO<sub>2</sub>NO<sub>2</sub> was observed at 940 cm<sup>-1</sup> which was assigned to the O-O stretch fundamental. The location of this band is required for calculation of a vibrational partition function for HO<sub>2</sub>NO<sub>2</sub>.

A correlation-based stabilization technique for use with the ALIAS spectrometer was developed and tested, and is currently implemented on the instrument. This software-based procedure allows long-term operation of the instrument without active temperature control of the laser cold head, and eliminates time consuming postflight data processing steps which were found to be necessary without the stabilization in place.

#### **E. Journal Publications**

1. R.D. May, "Absolute Linestrengths in the H<sub>2</sub>O<sub>2</sub>  $\nu_6$  Band," J. Quant. Spectrosc. Rad. Transfer, **45**, 267-272 (1991).
2. R.D. May and C.R. Webster, "Laboratory Measurements of NO<sub>2</sub> Line Parameters for the Interpretation of Stratospheric Spectra," Geophys. Res. Lett., **17**, 2157-2160 (1990).
3. R.D. May, "Correlation-Based Technique for Automated Tunable Diode Laser Scan Stabilization," Rev. Scient. Instrum. (accepted for publication).
4. R.D. May and D.B. Peterson, "Observation of the O-O Stretch Fundamental Band of HO<sub>2</sub>NO<sub>2</sub>," J. Molec. Spectrosc. (submitted for publication).
5. R.D. May, "Line Intensities and Collisional Broadening Parameters for the  $\nu_4$  and  $\nu_6$  Bands of COF<sub>2</sub>," (in preparation).



A. TITLE OF RESEARCH TASK

MILLIMETER AND SUBMILLIMETER SPECTROSCOPY  
OF  
MOLECULES OF ATMOSPHERIC IMPORTANCE

B. INVESTIGATORS AND INSTITUTIONS

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C. ABSTRACT OF RESEARCH OBJECTIVES

It has been demonstrated that remote sensing techniques based upon millimeter, submillimeter and far infrared (mm/submm/fir) technology can make important contributions to atmospheric science. The planning, execution, and interpretation of those experiments require a firm knowledge of the spectroscopic properties of atmospheric molecules. Our work is designed to support these atmospheric observations via contributions to the spectroscopic data base for the microwave through infrared spectral region. The work includes both the direct measurement of mm/submm/fir spectra of important atmospheric species and the calculation of synthetic spectra from these measurements. Results include line positions and linewidths in both the ground and excited vibrational states.

D. SUMMARY OF PROGRESS AND RESULTS

During this period we have carried out measurements of line positions, widths, and intensities in the millimeter, submillimeter, and far infrared spectral regions and have done theoretical calculations in support of these measurements. Species studied include  $\text{HNO}_3$ ,  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HDO}$ ,  $\text{HOOH}$ , and  $\text{N}_2\text{O}_5$ . Much of the work finished in this period is detailed in the "JOURNAL PUBLICATIONS" section below and can only be briefly summarized here.

Our earlier  $\text{N}_2\text{O}_5$  work (done in collaboration with B. P. Winnewisser and M. Winnewisser in Giessen, West Germany) has been extended. This work was originally motivated by a need for better information at long wavelengths so that the usefulness of these spectral regions for remote sensing of  $\text{N}_2\text{O}_5$  could be evaluated. Because a detailed understanding of the energy levels and linewidth parameters of this spectrally complex species is not available, the synthetic calculation of its spectral characteristics needed for a more quantitative assessment of remote sensing retrieval data is not possible. As a result, we have done a new series of measurements of lineshapes and intensities for this species for a series of representative atmospheric temperatures. In addition, at the lower temperatures,

rotational/torsional structure has been resolved, providing an opportunity for a more detailed analysis of its complex spectrum.

In order to contribute to both the pure rotational and rotational-vibrational data base for atmospherically significant species, we have continued our work on the rotational structure of excited vibrational states. Our most recent work has been on  $\text{HNO}_3$  and  $\text{HOOH}$ . Some of the former is described in one of the publications listed below. To date the work on  $\text{HOOH}$  has focused on the  $n = 1$  torsional state and a number of lines have been measured, assigned, and analyzed. This work is being done in collaboration with the infrared group of Flaud and Camy-Peyret in Paris. This group is actively involved in both US and European atmospheric science projects and our work is aimed at providing an integrated data base for the entire spectral region from the microwave through the infrared.

We have also carried out a number of studies of pressure broadening in these species. We have used a new collisionally cooled system which makes possible pressure broadening measurements over a wide temperature range. We have studied collisions both with the atmospherically significant  $\text{N}_2$  and  $\text{O}_2$  as well as with  $\text{He}$  and  $\text{H}_2$ , the latter providing a wider information base for the benchmarking of theoretical methods. Details of this work are provided in some of the publications described below. Some of these results are especially interesting because they can be related to relatively simple physical ideas.

#### E. JOURNAL PUBLICATIONS

T. M. Goyette and F. C. De Lucia, "The Millimeter and Submillimeter Wave Spectrum of the  $\nu_8 + \nu_9$  State of  $\text{HNO}_3$ ," *J. Mol. Spectrosc.* **139**, 241 (1990).

T. M. Goyette, W. L. Ebenstein, S. L. Shostak, and F. C. De Lucia, "The Pressure Broadening of  $\text{NO}_2$  in the Millimeter and Submillimeter Wave Spectral Region," *JQSRT* **43**, 365 (1990).

T. M. Goyette and F. C. De Lucia, "The Pressure Broadening of the  $3_{1,3} - 2_{2,0}$  Transition of Water between 80 K and 600 K," *J. Mol. Spectrosc.* **143**, 346 (1990).

T. M. Goyette, W. L. Ebenstein, and F. C. De Lucia, "Rotational and Vibrational Temperatures in a 77 K Collisionally Cooled Cell," *J. Mol. Spectrosc.* **140**, 311 (1990).

J. C. Pearson, T. J. Anderson, E. Herbst, F. C. De Lucia, and P. Helminger, "Millimeter and Submillimeter Wave Spectrum of Highly Excited States of Water," *Ap. J. Lett.*, in press (1991).

T. M. Goyette, W. Guo, F. C. De Lucia and P. Helminger, "Variable Temperature Pressure Broadening of  $\text{HNO}_3$  in the Millimeter Wave Spectral Region," *JQSRT*, in press (1991).

## **A. Title of Research Task**

Millimeter and Submillimeter Spectroscopy in Support of Upper Atmospheric Research

## **B. Investigators**

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## **C. Abstract of Research Objectives**

A program of millimeter and submillimeter spectroscopy research is conducted in support of upper atmospheric research. This includes laboratory studies, critical analysis of data from all available sources, generation of line list catalogs, and distribution of results to the field measurement community. The program involves the acquisition and analysis of molecular spectral parameters which are required for the interpretation of data from stratospheric measurements. The laboratory spectral measurements specifically support the JPL millimeter radiometer instruments. In order to take full advantage of spectroscopic techniques for quantitative atmospheric measurements, emphasis is placed on performing accurate line frequency, line width, and transition moment measurements. A large portion of the spectral data is also of value to other groups which use spectroscopic techniques for atmospheric measurements. This will be cataloged in a continuously upgraded millimeter data base and made available to interested users. This program also provides rotational spectra of ground and excited states of molecules whose infrared spectra are observed in the upper atmosphere. The fitting programs developed for this program are used to analyze vibrational spectra. In addition, this program provides valuable molecular structural and reaction product distribution information which has direct bearing on proposed mechanisms for polar ozone destruction.

## **D. Summary of Progress and Results**

A gas flow reactor - millimeter spectrometer system which had been used for the synthesis of ClO dimer has been improved by the addition of a temperature controlled sample cell and Stark plates. Cl<sub>2</sub>O<sub>3</sub> has been identified from the submillimeter spectrum of the products of the ClO + OClO reaction. The spectra of all four chlorine isotopic species have been assigned and structural parameters have been determined. These are consistent with a chlorine chlorate structure.

Further measurements of the millimeter spectra of products of the ClO self reaction have yielded stronger evidence that the major product at low temperature is ClOOCl which is implicated in polar ozone destruction. The dipole moments of Cl<sub>2</sub>O and ClOOCl have been determined. This allows

their concentrations to be more accurately monitored in millimeter spectroscopy studies of their reactions.

A new analysis of the rotational spectrum of  $\text{COF}_2$  and the  $\nu_2$  band infrared spectrum has been completed and published. High resolution infrared spectra as well as rotational spectra of the  $\nu_3$  and  $\nu_5$  states have been fitted. The analysis is being completed.

Millimeter spectra of  $^{16}\text{O}^{18}\text{O}$  and vibrationally excited  $\text{O}_2$  in the metastable  $a^1\Delta$  state have been obtained and analyzed.

The JPL "Microwave, Millimeter, and Submillimeter Spectral Line Catalog" has been released for distribution via the NSSDC at GSFC. Thirty new atmospheric species have been included. Twenty one earlier calculations of atmospheric species have been improved.

Measurements have been completed of the air broadened linewidths for the 206 and 184 GHz  $\text{O}_3$  lines to be observed by the UARS MLS instrument.

## E. Journal Publications

1. G. A. McRae and E. A. Cohen, "The  $\nu_2$  Band of  $\text{HOBr}$ ," *J. Mol. Spectrosc.*, **139**, 369 (1990).
2. H. M. Pickett, "The Fitting and Prediction of Vibration-Rotation Spectra with Spin Interactions," *J. Mol. Spectrosc.*, **148**, 371 (1991).
3. E. A. Cohen and W. Lewis-Bevan, "Further Measurements of the Rotational Spectrum of  $\text{COF}_2$ : Improved Molecular Constants for the Ground and  $\nu_2$  States," *J. Mol. Spectrosc.*, **148**, 378 (1991).

## **Tunable Far Infrared Studies of Molecular Parameters in Support of Stratospheric Measurements**

### **Investigators and Institutions:**

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Smithsonian Astrophysical Observatory, Cambridge, MA

I. G. Nolt, M. D. Vanek and J. V. Radostitz

NASA Langley Research Center, Hampton, VA

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### **Abstract of Research Objectives:**

The purpose of this research is to make precise, fully line-resolved measurements of molecular parameters that are necessary for the analysis of spectra obtained in far infrared field measurement programs. These measurements make it possible to accurately analyze the data from field measurements to obtain atmospheric concentration profiles of key trace gases involved in the ozone chemistry.

The research objectives include: measurements of pressure broadening of molecular lines of OH, O<sub>2</sub>, O<sub>3</sub>, HCl, and H<sub>2</sub>O, their temperature dependences and, when possible, the pressure-induced frequency shifts of the lines; measurements of line positions of radical species, such as HO<sub>2</sub>.

This research is done in collaboration with K. M. Evenson, National Institute for Standards and Technology, Boulder, CO, and D. A. Jennings, NASA Langley Research Center, Hampton, VA.

In the past year, research has also included spectroscopic and retrieval calculations performed in support of satellite-based atmospheric measurement programs - the Global Ozone Monitoring Experiment (GOME) and the SCanning Imaging Absorption spectroMeter for Atmospheric CHartography (SCIAMACHY) - as well as an airborne laser magnetic resonance experiment being developed by NOAA and NIST for measurement of tropospheric OH, HO<sub>2</sub> and O(<sup>3</sup>P).

### **Summary of Progress and Results:**

Progress to date in this research includes the following studies:

**OH** Our measurements of the pressure-broadening by N<sub>2</sub> and O<sub>2</sub> of the hyperfine-resolved OH lines at 118.46 cm<sup>-1</sup> have now been published. We have made measurements of the broadening, and its temperature dependence, of the lines at 83.869 cm<sup>-1</sup>, which are currently being analyzed.

**HO<sub>2</sub>** The positions of 13 rotational lines of HO<sub>2</sub> have been measured between 2.5 and 5.9 THz (80 to 200 cm<sup>-1</sup>), including transitions from levels with K<sub>a</sub> as high as 5, providing the extension in K<sub>a</sub> necessary for proper refitting of the rotational Hamiltonian in order to develop the HO<sub>2</sub> database for atmospheric measurements. A parameterized Hamiltonian fitting program has been obtained and adapted to the HO<sub>2</sub> analysis. Final fitting of the Hamiltonian is currently underway.

**HCl** Our pressure-broadening study of the 2.5 THz line of H<sup>35</sup>Cl has now been published.

- HI** We have made measurements of the quadrupole-resolved rotational spectrum of HI up to the  $R_{11}$  lines. HI is of general spectroscopic interest, particularly since it provides a good example of the rotational dependence of the nuclear quadrupole coupling.
- O<sub>2</sub>** We have published a critical study on the use of O<sub>2</sub> magnetic dipole- allowed rotation lines for the calibration of far infrared atmospheric measurements.
- O<sub>3</sub>** The N<sub>2</sub> and O<sub>2</sub> broadening coefficients, and their temperature dependences over the 200-300 K range, of the O<sub>3</sub> line at  $114.47\text{ cm}^{-1}$  have been measured and are currently being analyzed.
- H<sub>2</sub>O** The N<sub>2</sub> and O<sub>2</sub> broadening coefficients, and their temperature dependences over the 200-300 K range, of the H<sub>2</sub>O line at  $88.65\text{ cm}^{-1}$  have been measured and are currently being analyzed.

Additional progress includes the decision to fly the GOME instrument on ESA's ERS-2 satellite in 1994, and the selection of SCIAMACHY for the ESA POEM-1 polar platform. Studies are currently underway exploring, among other aspects of these instruments, their ability to map the distribution of tropospheric ozone.

#### **Publications:**

Pressure Broadening of the  $118.455\text{ cm}^{-1}$  Rotational Lines of OH by H<sub>2</sub>, He, N<sub>2</sub>, and O<sub>2</sub>, K. V. Chance, D. A. Jennings, K. M. Evenson, M. D. Vanek, I. G. Nolt, J. V. Radostitz, and K. Park, *Journal of Molecular Spectroscopy* 146, 375-380, 1991.

On the Use of O<sub>2</sub> Spin-Rotation Lines for Elevation Angle Calibration of Atmospheric Thermal Emission Spectra, K. V. Chance, W. A. Traub, K. W. Jucks, and D. G. Johnson, *International Journal of Infrared and Millimeter Waves* 12, 581-588, 1991.

Pressure Broadening of the 2.5 THz H<sup>35</sup>Cl Rotational Line by N<sub>2</sub> and O<sub>2</sub>, K. Park, K. V. Chance, I. G. Nolt, J. V. Radostitz, M. D. Vanek, D. A. Jennings, and K. M. Evenson, *Journal of Molecular Spectroscopy* 147, 521-525, 1991.

Retrieval and Molecule Sensitivity Studies for the Global Ozone Monitoring Experiment and the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY, K. V. Chance, J. P. Burrows, and W. Schneider, *Proc. S.P.I.E., Vol. 1491, Remote Sensing of Atmospheric Chemistry*, ed. R. J. McNeal, 1991.

Scanning Imaging Absorption Spectrometer for Atmospheric ChartographY, J. P. Burrows and K. V. Chance, *Proc. S.P.I.E., Vol. 1490, Future European and Japanese Remote Sensing Senors and Programs*, ed. P. N. Slater, 1991.

## FAR INFRARED SPECTROSCOPY of ATMOSPHERIC ATOMS and MOLECULES

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### ABSTRACT

Ultra high resolution far Infrared laser spectra of atmospheric atoms and molecules yield accurate frequencies of their rotational transitions, accurate broadening coefficients, and pressure induced frequency shifts. The frequencies are used to identify these species in the atmosphere, and the broadening coefficients are used in determining their absolute concentrations. Two different spectroscopic techniques are used: laser magnetic resonance (LMR) and tunable far infrared (TuFIR) spectroscopy.

### PROGRESS AND RESULTS

Far infrared spectra of atmospheric molecules are used to identify species whose atmospheric emission spectra have been observed. Researchers at Harvard College Observatory and at Istituto di Ricerca Elettromagnetica CNR, Italy are making such measurements using high altitude balloon borne Fourier transform spectrometers. In support of their observations,  $O_2$ , OH,  $HNO_3$ , CO, HCl, HF, and HD spectra have previously been measured in our laboratory. During the past two years, frequencies of  $^{12}C^{16}O$  (IR),  $^{13}C^{16}O$ , the O atom, and a highly accurate set of FIR frequencies of CO were published (1,2,6,&7). Publications on  $HO_2$  and HI spectra are in preparation.

Line broadening coefficients have been determined for a number of different transition of various molecules with various collisional partners. These coefficients are necessary to determine the absolute concentrations of the molecule from its emission spectra. The data is also used in determining the pointing direction of the telescopes used in taking the upper atmospheric emission data. Previously, OH transitions and an important  $O_2$  transition were measured. In the past two years, measurements of broadening of various transitions of OH, HCl, and  $CH_3CN$  have been completed and published (5, 8, & 9).

We plan to extend the spectral frequency measurements to water, ozone, and methyl alcohol and to measure the broadening coefficients of a number of atmospheric molecules including temperature dependences of some.

## PUBLICATIONS

1. Laser Heterodyne Frequency Measurements of  $^{12}\text{C}^{16}\text{O}$ , M. Schneider, K.M. Evenson, M.D. Vanek, D.A. Jennings, J.S. Wells, and W. Urban, J. Mol. Spectrosc., 135, 197-206 (1989).
2.  $^{12}\text{C}^{16}\text{O}$  Laser Frequency Tables for the 34.2 to 62.3 THz (1139 to 2079  $\text{cm}^{-1}$  Region, M. Schneider, K.M. Evenson, M.D. Vanek, D.A. Jennings, J.S. Wells, A. Stahn, and W. Urban, NBS Tech Note 1321 (1989).
3. Rotational Far Infrared Spectrum of  $^{13}\text{CO}$ , L. R. Zink, P. DeNatale, F. S. Pavone, M. Prevedelli, K. M. Evenson, and M. Inguscio, J. Mol. Spectrosc., 143, 304-310 (1990).
4. High Resolution Far Infrared Spectroscopy, L. R. Zink, M. Prevedelli, K. M. Evenson, and M. Inguscio, NATO ASI School: Laser Spectroscopy, Ed. H. Walther and M. Inguscio, Sept. 1989, San Miniato, Italy.
5. Pressure Broadening of the 3.551 THz Rotational Lines of OH by  $\text{H}_2$ , He,  $\text{N}_2$ , and  $\text{O}_2$ , K. V. Chance, D. A. Jennings, K. M. Evenson, M. D. Vanek, I. G. Nolt, J. V. Radostitz, and K. Park, J. of Mol. Spectrosc., 146, 375-380 (1990).
6. Tunable Far Infrared Measurement of Atomic Oxygen Fine Structure Splittings, L. R. Zink, K. M. Evenson, F. Matsushima, T. Nelis, and R. Robinson, Astro Phys. Jour. Lett., 371, L85-L86 (1991).
7. Accurate Far-Infrared Rotational Frequencies of Carbon Monoxide, T. D. Varberg and K. M. Evenson, to be published in Astro Physical Journal, Feb. 1992.
8. Pressure Broadening of the 2.5 THz  $\text{H}^{35}\text{Cl}$  Rotational Line by  $\text{N}_2$  and  $\text{O}_2$ , K. Park, K.V. Chance, I. G. Nolt, J. V. Radostitz, M. D. Vanek, D. A. Jennings, and K. M. Evenson, J. Mol. Spectrosc. 147, 521-525 (1991)
9. Far Infrared Self-Broadening in Methylcyanide: Absorber-Perturber Resonance, G. Buffa, O. Tarrini, P. De Natale, M. Inguscio, F. S. Pavone, M. Prevedelli, K. M. Evenson, L. R. Zink, and G. W. Schwaab, submitted to Infrared Physics.



**A. Title:** Laboratory Studies of Vibration-Rotation Lineshapes of Atmospheric Constituents

**B. Investigator and Institution:**

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**C. Abstract of Research Objectives**

The purpose of this research is to improve our understanding of the spectra of atmospheric constituents important for satellite remote sensing. In particular, investigations that support the CLAES (Cryogenic Limb Array Etalon Spectrometer) and ISAMS (Improved Stratospheric and Mesospheric Sounder) instruments on UARS (Upper Atmosphere Research Satellite) are being pursued. One of the main goals of this work is to study the  $791\text{ cm}^{-1}$  Q branch of  $\text{CO}_2$  used by CLAES for temperature retrievals. Particular attention is being paid to the effects of line mixing on this Q branch and on other  $\text{CO}_2$  bands. Most of the Q branch experimental studies are performed with a tunable diode laser spectrometer.

**D. Summary of Progress and Results**

Our previous studies of self-broadened line mixing in the  $791\text{ cm}^{-1}$  Q branch of  $\text{CO}_2$ , used by CLAES on the UARS satellite for temperature and pressure sounding, showed excellent agreement with a theory that uses a scaling law approximation for describing rotational relaxation. We have found that the same is not true for  $\text{N}_2$ -broadened spectra that will be observed by CLAES. The scaling law we used for self-broadening significantly underestimates the amount of line mixing in the  $\text{N}_2$ -broadened spectra. This underestimation of mixing was removed in our calculations by varying the relaxation rate for  $f \rightarrow e$  and  $f \rightarrow f$  collisions in the  $\Pi$  state. These collision rates appear to be equal for  $\text{CO}_2$ - $\text{CO}_2$  collisions, but not for  $\text{CO}_2$ - $\text{N}_2$  collisions.

We have also recorded spectra, both self and  $\text{N}_2$ -broadened, in the  $740\text{ cm}^{-1}$  Q-branch of  $\text{CO}_2$ , which is part of a  $\Delta$ - $\Pi$  band. Consequently both vibrational states involved in these transitions contain vibrational angular momentum. Calculations of line mixing for this Q-branch were not able to reproduce the measured spectra if  $f \rightarrow e$  and  $f \rightarrow f$  collision rates in both states are kept equal. This was true for self- as well as  $\text{N}_2$ -broadened spectra. Good agreement is only possible if we vary these collision rates between the two vibrational sub-states.

We previously reported that ab-initio calculations of line mixing in  $\text{CO}_2$  Q-branches broadened by He agreed well with our phenomenological theory but not with the observed spectra. We have been able to get good agreement between the phenomenological theory and experiment by requiring relaxation to the  $f$  sub-level in the  $\Pi$  state be three times more likely than relaxation to the  $e$  vibrational sub-level.

The ATMOS spectra recorded on Spacelab 3 provide an excellent test of our line mixing theories because they have high optical depths in the Q-branch wings where mixing is most evident and because they are formed by absorption over a wide range of temperatures. In collaboration with David Edwards at NCAR, we have compared calculated and observed ATMOS spectra in the  $618$  and  $791\text{ cm}^{-1}$  regions. We obtained excellent results in regions where line mixing was strong, if we used the relative  $f \rightarrow e$  and  $f \rightarrow f$  collision rates derived from laboratory spectra. We also modeled radiative transfer for the CLAES instrument and found that the neglect of line mixing could cause errors in equivalent brightness temperatures as large as  $10\text{K}$ . This fact underscores the importance of line mixing for the CLAES

temperature retrieval algorithms, which have expected accuracies on the order of 1K. We found the effect of line mixing on the ISAMS channels to be much less, on the order of 2K.

**E. Journal Publications (1990-1991):**

D. P. Edwards and L. L. Strow, **Spectral Line Shape Considerations for Limb Temperature Sounders**, accepted for publication, J. Geophys. Res., July 1991.

## Collisional Lineshapes and Molecular Beam Spectroscopy of Atmospheric Molecules

Principal Investigator: Alan S. Pine

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Principal Collaborators: G.T. Fraser and J.P. Looney, (NIST)

### Objectives:

The purposes of this program are to study collisional lineshapes and to obtain molecular beam spectra of various atmospheric molecules of interest to the NASA UARS (Upper Atmosphere Research Satellite), ATMOS (Atmospheric Trace Molecule Spectroscopy) and HALOE (Halogen Occultation Experiment) projects. The pressure broadenings, shifts and line profiles are required for quantitative monitoring of the distribution of contaminant gases and for temperature sounding of the atmosphere. Many of the molecular species of interest exhibit marked deviations in lineshape from the simple Lorentzian or Voigt profiles usually employed to model the spectral absorptions. A number of physical phenomena contribute to these lineshape distortions including collisional (Dicke) narrowing, speed-dependent collisional cross sections, non-impact (finite collision time) behavior, and collisional interferences (line coupling or line mixing). The precise measurement of these line profiles requires very high resolution infrared instrumentation such as the tunable difference-frequency-laser system and the color-center-laser photoacoustic spectrometer at NIST. Some of the heavier atmospheric molecules exhibit extremely dense, often strongly perturbed, spectra at normal atmospheric temperatures which have not been analyzed even with Doppler-limited resolution. In these cases molecular beam techniques can provide initial assignments due to sub-Doppler resolution and the considerable spectral simplification from the very low effective temperatures in an adiabatic expansion.

### Summary of Progress:

Q-Branch Line Mixing: We have recorded three Q-branches of HCCH ( $\nu_1+\nu_5$  at  $4091\text{ cm}^{-1}$ ,  $\nu_3+\nu_4$  at  $3897\text{ cm}^{-1}$ , and  $\nu_2+2\nu_4+\nu_3$  at  $3881\text{ cm}^{-1}$ ) and of HCN ( $\nu_1+\nu_2$  at  $4004\text{ cm}^{-1}$ ,  $\nu_2+\nu_3$  at  $2806\text{ cm}^{-1}$ , and  $\nu_1-\nu_2$  at  $2599\text{ cm}^{-1}$ ) using transmission spectroscopy with a difference-frequency laser system. The spectral profiles were examined from the Doppler limit at low pressures to the heavily overlapped regime at pressures approaching one atmosphere. The contours of these Q branches exhibit non-additive behavior in that they cannot be fit with a direct superposition of Lorentzian lines with the known intensities and positions of the components. Superposition deviations in the absorption constants are most evident near the band head and wings where most temperature sounding and monitoring is performed. These deviations arise from collisional line coupling when collisions can transfer intensity between overlapping lines in the spectra. Inelastic collisions that transfer population to states not involved in the overlapped transitions lead to normal superposable broadening. Since the Q branches in linear molecules access only one vibrational "parity" (f level) component of doublet  $\Pi$  levels, we find that  $f \leftrightarrow f$  conserving collisions result in line mixing while  $f \leftrightarrow e$  contribute only broadening. Additional restrictions on the off-diagonal relaxation matrix elements have been imposed empirically to reduce the amount of line coupling observed, which will require

further theoretical justification and experimental verification. This decoupling is twice as large in the nonpolar HCCH species than in the strongly polar HCN molecule, but is otherwise independent of vibration and pressure. The HCN broadening coefficients and Q-branch profiles require a more sophisticated collision-dynamic scaling law to fit the data than do HCCH.

Line Broadening in Methane: Self-,  $N_2$ -,  $O_2$ -,  $H_2$ -, He- and Ar-broadening spectra of the Q branch of the  $\nu_3$  fundamental of  $CH_4$  near  $3019\text{ cm}^{-1}$  have been recorded with a difference-frequency laser spectrometer at  $T=296\text{ K}$ . Since this is a very irregular Q branch exhibiting tetrahedral splittings and much blending of lines, new fitting procedures are being developed to process the data in order to extract the broadening and shifting coefficients and to test for line mixing.

Molecular-Beam Optothermal Spectroscopy: The  $\nu_1$  OH stretching fundamental bands of methanol ( $CH_3OH$ ) and nitric acid ( $HNO_3$ ) have been recorded at high resolution ( $\sim 15\text{ MHz FWHM}$ ) and low temperatures ( $\sim 10\text{ K}$ ) using a color-center-laser-excited, bolometer-detected molecular beam. Microwave-infrared double resonance was used to obtain initial definitive assignments. The  $CH_3OH$  spectrum has been fully analyzed, yielding an anomalous increase in the torsional barrier in the excited OH stretch and several perturbing states involving combinations of CH stretches and torsional overtones. The  $HNO_3$  spectrum has been mostly assigned and is under analysis by A.G. Maki. Spectra have also been recorded of the CH stretching bands of the hydrofluorocarbons  $CHF_2Cl$  (HCFC-22) and  $CH_3CF_3$  (HFC-143a) of which the former has been analyzed, including two strong perturbations, and the latter is so far uninterpreted. New high precision spectra of benzene,  $C_6H_6$ , in the  $\nu_{12}$  band at  $3048\text{ cm}^{-1}$  and the  $\nu_{14}$  band at  $1038\text{ cm}^{-1}$  have been obtained, the latter using a recently constructed  $CO_2$ -laser-microwave-sideband system for excitation.

#### Publications:

1. Decoupling in the line mixing of acetylene infrared Q branches.  
A.S. Pine and J.P. Looney, J. Chem. Phys. 93, 6942 (1990).
2. Self-broadening and line mixing in HCN Q Branches.  
A.S. Pine and J.P. Looney, J. Chem. Phys., submitted.
3. Molecular-beam optothermal spectrum of the OH stretching band of methanol.  
I. Kleiner, G.T. Fraser, J.T. Hougen and A.S. Pine, J. Mol. Spectrosc. 147, 155 (1991).
4. Molecular-beam optothermal spectroscopy of the  $9.6\text{ }\mu\text{m}$   $\nu_{14}$  band of benzene.  
M-L. Junttila, J.L. Domenech, G.T. Fraser and A.S. Pine, J. Mol. Spectrosc. 147, 513 (1991).
5. Molecular-beam spectrum of the  $3.3\text{ }\mu\text{m}$   $\nu_{12}$  band of benzene.  
J.L. Domenech, M-L. Junttila and A.S. Pine, J. Mol. Spectrosc. 149, in press.
6. Molecular-beam spectrum of the  $\nu_1$  CH stretch of  $CHF_2Cl$  (HCFC-22).  
G.T. Fraser, J.L. Domenech, M-L. Junttila and A.S. Pine, in preparation.

## NASA Upper Atmosphere Research Program

### RESEARCH SUMMARY 1990-1991

#### A. TITLE OF RESEARCH TASK

"A Facility for High Resolution Spectroscopy: Laboratory and Ground Based Observations in Support of Upper Atmospheric Research"

#### B. INVESTIGATORS AND INSTITUTIONS

Principal Investigator: James W. Brault (National Solar Observatory)

Visiting Investigators:

Jet Propulsion Laboratory	Langley Research Center	Goddard Space Flight Center
L. R. Brown	C. Rinsland	J. J. Hillman
E. Cohen	M. A. H. Smith	D. E. Jennings
J. S. Margolis		T. Kostiuik
H. Pickett	Ames Research Center	
R. Poynter		
R. Toth	C. Chackerian	

#### C. ABSTRACT OF RESEARCH OBJECTIVES

This research task consists of operating a *facility* for making spectroscopic observations in support of upper atmospheric research. The facility responds to the needs and interests of the visiting investigators. Therefore, the research objectives are not predetermined except in broad outline. The emphasis is on studies that take advantage of the particular strengths of the Fourier transform spectrometer on Kitt Peak: high spectral resolution combined with wide spectral range and low noise.

#### D. SUMMARY OF PROGRESS, RESULTS AND PROPOSED WORK

JPL investigators L. R. Brown, J. S. Margolis, R. L. Poynter and R. A. Toth use the FTS to record high resolution infrared laboratory spectra to support ongoing remote sensing of the Earth's atmosphere by spectroscopy. Interactive analysis of the spectra are done using customized software developed at JPL for use at the Atmospheric Trace Molecule Spectroscopy (ATMOS) Data Analysis Facility. The results are made available in computer-readable format to provide improved molecular line parameters for the international databases such as the HITRAN and GEISA, as well as local databases at JPL, Langley, Goddard and other laboratories requiring such information. Currently, the line positions, line strengths, and lower state energies of important atmospheric species such as  $\text{H}_2\text{O}$ ,  $\text{HDO}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{NO}_2$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{NH}_3$ , and  $\text{COF}_2$  are being obtained. In addition, the collision-broadened line widths and shifts are being measured for  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{NH}_3$ .

During FY90 and 91, accurate measurements of line positions and strengths were obtained for  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ ,  $\text{H}_2^{18}\text{O}$ ,  $\text{HDO}$  and  $\text{D}_2\text{O}$  in the region from 900 to  $4500\text{ cm}^{-1}$ . A quantum mechanical model for the dipole moment was developed and applied successfully to the line strength measurements in the  $\nu_2$  bands of  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{17}\text{O}$  and  $\text{H}_2^{18}\text{O}$ . An analysis of line

positions of five bands of  $^{13}\text{CH}_4$  in the 2200 to 3200  $\text{cm}^{-1}$  region was begun as the first step in a comprehensive reinvestigation of that region. To support interpretation of the HALO data in the HF channel, a study to determine the lower state energies of  $\text{CH}_4$  from 3900 to 4200  $\text{cm}^{-1}$  started, using new spectra recorded at reduced sample temperatures between 185K and 270K. Ongoing theoretical modeling of interacting bands of  $\text{H}_2\text{O}$  from 2800 to 4500  $\text{cm}^{-1}$ ,  $\text{COF}_2$  at 1940  $\text{cm}^{-1}$  and  $\text{CH}_4$  from 2200 to 3300  $\text{cm}^{-1}$  and analysis of line strengths and widths of  $\text{CH}_3\text{Cl}$  at 7  $\mu\text{m}$  and  $\text{NH}_3$  at 2  $\mu\text{m}$  were pursued.

The laboratory spectroscopy group at NASA Langley Research Center has used the McMath FTS to record high-quality spectra of pure ozone and ozone-air mixtures at a series of temperatures from room temperature down to  $-63^\circ\text{C}$ . The spectra cover several absorption bands in the 4 to 15  $\mu\text{m}$  region, and are being analyzed to determine the behavior of pressure broadening and shift coefficients at low temperatures typical of those found in the upper atmosphere. Spectra of mixtures of  $\text{H}_2\text{O}$ ,  $\text{HDO}$ , and  $\text{D}_2\text{O}$  in air,  $\text{N}_2$ , or  $\text{O}_2$  at room temperature were also recorded in 1990; analyses of broadening and shifts of  $\text{HDO}$  and  $\text{D}_2\text{O}$  lines in these spectra have been completed.

Methane spectra recorded by the Langley group in previous years have been analyzed to determine  $\text{N}_2$ -,  $\text{O}_2$ -,  $\text{Ar}$ -, and air-broadening coefficients and pressure-induced line shifts for a large number of absorption lines belonging to several different vibration-rotation bands. This work includes the determination of  $\text{N}_2$ - and air-broadening and shift coefficients in the 8  $\mu\text{m}$  region over the same temperature range as the 1990-1991 ozone spectra. Some of the results have already been applied in analyses of atmospheric data.

Continuing analysis of ozone absorption spectra recorded by the Langley group in 1984, 1985, 1987, and 1989 has resulted in improved line positions, intensities, and assignments for numerous bands in the 2.5 to 15  $\mu\text{m}$  region. Analyses of self-broadening coefficients for lines in the 5 to 15  $\mu\text{m}$  region, and  $\text{N}_2$ -,  $\text{O}_2$ -, and air-broadening coefficients and pressure-induced line shifts in the 3  $\mu\text{m}$  region have also been completed.

## E. JOURNAL PUBLICATIONS

- Camy-Peyret, C., J. -M. Flaud, C. P. Rinsland, M. A. H. Smith, V. Malathy Devi and A. Goldman, "Line Parameters for Ozone Hot Bands in the 4.8- $\mu\text{m}$  Spectral Region," *J. Mol. Spectrosc.* **139**, 353-360 (1990).
- Camy-Peyret, C., J. -M. Flaud, M. A. H. Smith, C. P. Rinsland, V. Malathy Devi, J. J. Plateaux and A. Barbe, "The 3.3- $\mu\text{m}$  Bands of Ozone: Line Positions and Intensities," *J. Mol. Spectrosc.* **141**, 134-144 (1990).
- Flaud, J. -M., C. Camy-Peyret, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith and A. Goldman, "Improved Line Parameters for Ozone Bands in the 10- $\mu\text{m}$  Spectral Region," *Appl. Opt.*, **29**, 3667-3671 (1990).
- Flaud, J. -M., C. Camy-Peyret, C. P. Rinsland, M. A. H. Smith, and V. Malathy Devi, "Atlas of Ozone Spectral Parameters from Microwave to Medium Infrared," Academic Press, Cambridge, Massachusetts (1990).
- Jouvard, J. M., B. Lavorel, J. P. Champion, and L. R. Brown, "Preliminary Results on the Analysis of the Pentad of  $^{13}\text{CH}_4$ ," The 45th Symposium on Molecular Spectroscopy, Abstract TF14, Ohio State Univ. (1990) and a paper is in preparation.
- Malathy Devi, V., A. Perrin, J. -M. Flaud, C. Camy-Peyret, C. P. Rinsland and M. A. H. Smith, "Line Positions and Intensities for the  $\nu_2+3\nu_3$  Band of  $^{16}\text{O}_3$  Around 2.7  $\mu\text{m}$ ," *J. Mol. Spectrosc.*, **143**, 381-388 (1990).
- Margolis, J. S., and R. L. Poynter, "Low Temperature Hydrogen Broadened Linewidths of Ammonia in the (0,1,0,0) - (0,0,0,0) Band," *Appl. Opt.*, **30**, 3203 (1991).

- Margolis J. S., R. L. Poynter, and L. R. Brown, "Line Parameters of Ammonia in the Infrared," Second International Conference on Laboratory Research for Planetary Atmospheres, 21 Oct. 1990, Charlottesville Va.
- Margolis, J. S., "The Collisional Broadening and Shifting of Methane Lines by Hydrogen in the 4125 to 4280  $\text{cm}^{-1}$  Region," (in preparation).
- Perrin, A., A. -M. Vasserot, J. -M. Flaud, C. Camy-Peyret, C. P. Rinsland, M. A. H. Smith and V. Malathy Devi, "The  $\nu_2$  Bands of  $^{18}\text{O}_3$ ,  $^{18}\text{O}^{16}\text{O}^{18}\text{O}$ , and  $^{16}\text{O}^{18}\text{O}^{18}\text{O}$ : Line Positions and Intensities," *J. Mol. Spectrosc.* **143**, 311-317 (1990).
- Perrin, A., A. -M. Vasserot, J. -M. Flaud, C. Camy-Peyret, V. Malathy Devi, M. A. H. Smith, C. P. Rinsland, A. Barbe, S. Bouazza and J. J. Plateaux, "The 2.5  $\mu\text{m}$  Bands of Ozone: Line Positions and Intensities," *J. Mol. Spectrosc.*, in press (1991).
- Rinsland, C. P., L. R. Brown, and C. B. Farmer, "Infrared Spectroscopic Detection of Sulfur Hexafluoride ( $\text{SF}_6$ ) in the Lower Stratosphere and Upper Troposphere," *J. Geophys. Res.*, **95**, 5577-5585 (1990).
- Rinsland, C. P., M. R. Gunson, J. C. Foster, R. A. Toth, R. Zander, and J. S. Namkung, "Stratospheric Profiles of Heavy Water Vapor Isotopes and  $\text{CH}_3\text{D}$  From Analysis of the ATMOS Spacelab 3 Infrared Solar Spectra," *J. Geophys. Res.*, **96**, 1057-1068 (1991).
- Rinsland, C. P., M. A. H. Smith, V. Malathy Devi, J. -M. Flaud and C. Camy-Peyret, "The  $2\nu_2 + \nu_3$  and  $2\nu_2 + \nu_1$  Bands of  $^{16}\text{O}_3$  at 4.1  $\mu\text{m}$ : Line Positions and Intensities," *J. Mol. Spectrosc.*, **139**, 343-352 (1990).
- Rinsland, C. P., M. A. H. Smith, V. Malathy Devi, A. Perrin, J. -M. Flaud and C. Camy-Peyret, "The  $\nu_2$  Bands of  $^{16}\text{O}^{17}\text{O}^{16}\text{O}$  and  $^{16}\text{O}^{16}\text{O}^{17}\text{O}$ : Line Positions and Intensities," *J. Mol. Spectrosc.*, in press (1991).
- Rinsland, C. P., M. A. H. Smith, V. Malathy Devi and D. C. Benner, "Measurements of Lorentz-broadening Coefficients and Pressure-induced Line Shift Coefficients in the  $\nu_2$  Band of  $\text{D}_2^{16}\text{O}$ ," *J. Mol. Spectrosc.*, in press (1991).
- Rinsland, C. P., M. A. H. Smith, V. Malathy Devi and D. C. Benner, "Measurements of Lorentz-broadening Coefficients and Pressure-induced Line Shift Coefficients in the  $\nu_2$  Band of  $\text{HD}^{16}\text{O}$ ," Manuscript submitted to *J. Mol. Spectrosc.* (1991).
- Rinsland, C. P., A. Goldman, M. A. H. Smith and V. Malathy Devi, "Measurements of Lorentz Air-broadening Coefficients and Relative Intensities in the  $\text{H}_2^{16}\text{O}$  Pure Rotational and  $\nu_2$  Bands from Long Horizontal Path Atmospheric Spectra," *Appl. Opt.*, **30**, 1427-1437 (1991).
- Smith, M. A. H., C. P. Rinsland and V. Malathy Devi, "Measurements of Self-broadening of Infrared Absorption Lines of Ozone," *J. Mol. Spectrosc.*, **147**, 142-154 (1991).
- Toth, R. A., "Line Frequencies Measurements and Analysis of  $\text{N}_2\text{O}$  Between 900 - 4700  $\text{cm}^{-1}$ ," *Appl. Opt.* (in press).
- Toth, R. A., "The  $\nu_2$  band of  $\text{H}_2^{16}\text{O}$  - Line Strengths and Transition Frequencies," *J. Opt. Soc. Am. B* (in press).
- Toth, R. A., "Transition Frequencies and Absolute Strengths of  $\text{H}_2^{18}\text{O}$  and  $\text{H}_2^{17}\text{O}$  in the 6.2  $\mu\text{m}$  Region," *J. Opt. Soc. Am. B* (submitted).
- Toth, R. A., "High Resolution Measurements and Analysis of  $^{14}\text{NO}_2$  in the (001)-(000) and (0110)-(010) Bands," (in preparation).

## Task Summary, August 1991

A. Title: Calibration Facilities for NASA Payloads at SURF II

B. Principal Investigator: Robert P. Madden

Institution: U. S. Department of Commerce  
National Institute of Standards and Technology  
Electron and Optical Physics Division

### C. Abstract of Research Objectives

It is critically important to have a common radiometric base for the wide range of scientific missions being carried out by rocket, by satellite, and on the space shuttle. It has been demonstrated that this can be achieved by utilizing the NASA Spectrometer Calibration Facility beamline at SURF II, the Synchrotron Ultraviolet Radiation Facility at the National Institute of Standards and Technology. Synchrotron radiation, which has a calculable nature, serves as a primary irradiance standard used to calibrate spectrometer and photometer systems over a wide range of wavelengths. Two calibration stations provide fine control of motions of instruments mounted in their gimbals mounts, one station being located inside the large spectrometer calibration vacuum chamber for simulation of space conditions. The accuracy of this calibration source has been thoroughly documented and is well suited to this task.

### D. Summary of Progress and Results:

During the 1990-91 period 17 separate instrument calibrations were performed. Users included: J. Mentall (two times), GSFC (rocket spectrometers); G. Rottman/T. Woods (four times), LASP (UARS-SOLSTICE and EUV Spectrometers); R. Thomas (two times), GSFC (grating calibrations); G. Brueckner/M. VanHoosier/J. Lean (three times), NRL (UARS-SUSIM and ATLAS-SUSIM); D. Judge, USC-SSC (EUV Spectrometer). These included the final pre-flight calibrations of the UARS SUSIM and SOLSTICE instruments which are part of the upcoming space shuttle mission scheduled for launch September 12, 1991.

Improvements to the Spectrometer Calibration Facility included major changes to the motion control systems for the two calibration stations. A new computer system with higher speed interface was acquired as well as a backup which also serves as a remote control computer station. Software was written which now provides an easier to use graphical interface for the control of the motor drives and readout of the encoder positions for yaw, pitch, horizontal, and vertical motions of each of the two stations. Also new linear encoders for the pitch and yaw motions have been installed at the two stations. These encoders provide direct indications of motions of the gimbals rather than the indirect readings from the shaft encoders used previously. The shaft encoders have been incorporated into the new system as backups. A new baking system was installed in the large compound bellows which couples the spectrometer calibration chamber to the rest of the beamline.



## E. Journal Publications

T. N. Woods and G. J. Rottman, "Solar EUV Irradiance Derived from Rocket Experiments on 10 Nov. 1988," J. Geophysics Research (1990).

R. P. Madden, R. Canfield, M. Furst, A. Hamilton, L. Hughey, "SURF II - Characteristics, Facilities, and Plans, submitted for publication in Review of Scientific Instruments (1991).

Additional talks given during this period include:

J. Lean, "Calibration of SUSIM/UARS Experiment," Workshop on Extreme Vacuum Ultraviolet Radiometry for Solar and Terrestrial Physics, Berlin, Germany, October 22-23, 1990.

M. L. Furst, "Spectrometer Calibrations at SURF-II," a talk presented at the Infrared Background Signature Survey (IBSS) Data Management Review #3, Nichols Research Corp, Rosslyn, VA, February 7, 1991.

J. Lean, M. VanHoosier, and G. Brueckner, "SUSIM: A Program to Measure Changes in the Sun's Ultraviolet Spectral Irradiance over Solar Cycle Time Scale," Solar Physics Division Meeting, Huntsville, AL, April 9-11, 1991.

R. P. Madden, "UV Irradiance Standards," a talk presented at the 1991 CORM Annual Meeting and Conference, Gaithersburg, MD, May 21, 1991.

J. Lean and M. VanHoosier, "Spectral Irradiance Comparison of UV Sources," a talk presented at the 1991 CORM Annual Meeting and Conference, Gaithersburg, MD, May 21, 1991.

R. P. Madden, R. Canfield, M. Furst, A. Hamilton, L. Hughey, "SURF II - Characteristics, Facilities, and Plans," 4th International Conference on Synchrotron Radiation Instrumentation, Chester, England, July 15-19, 1991.

# Analysis of Atmospheric Spectra for Trace Gases

## Investigators and Institutions

P.I.: Curtis P. Rinsland, NASA Langley Research Center  
Co.-I's: Dr. Mary Ann H. Smith, NASA Langley Research Center  
Dr. Aaron Goldman, University of Denver  
Dr. David G. Murcray, University of Denver  
Dr. Frank J. Murcray, University of Denver

## Abstract of Research Objectives

The objective of this work is the comprehensive analysis of high-resolution atmospheric spectra recorded in the mid-IR to obtain simultaneous measurements of coupled parameters (gas concentration profiles, total column amounts, pressure, and temperature) in the stratosphere and upper troposphere and long-term trends of key trace gases. Solar absorption spectra recorded with the University of Denver group's balloon-borne and ground-based interferometers and solar spectra recorded from Kitt Peak since 1977 are used in the analyses.

## Summary of Progress and Results

Circa 1980 stratospheric solar occultation spectra recorded by the University of Denver spectroscopy group have been compared with data from their recent balloon flights and the 1985 ATMOS/Spacelab 3 results to deduce the long-term accumulation rates of carbonyl fluoride ( $\text{COF}_2$ ), chlorofluorocarbon 22 ( $\text{CHClF}_2$ ), and sulfur hexafluoride ( $\text{SF}_6$ ) in the lower stratosphere over the last decade. Consistent sets of line parameters and spectral calibration methods have been used in the retrievals. Assuming exponential increases with time, the average accumulation rates derived from the data are  $(10.3 \pm 1.8)\% \text{ yr}^{-1}$  for  $\text{COF}_2$  between October 1979 and April 1989,  $(9.4 \pm 1.3)\% \text{ yr}^{-1}$  for  $\text{CHClF}_2$  between March 1981 and June 1988, and  $(7.4 \pm 1.9)\% \text{ yr}^{-1}$  for  $\text{SF}_6$  between March 1981 and June 1988. As part of this work, calculations of the trends were performed by M. K. W. Ko and N. D. Sze with the Atmospheric and Environmental Research (AER) one-dimensional model and compared with the measurements.

More than 300  $\sim 0.01 \text{ cm}^{-1}$  resolution solar absorption spectra recorded from Kitt Peak have been analyzed to deduce total column amounts of HF on 93 different days and HCl on 35 different days between 1977 and 1990. The results are based on the analysis of the HF and  $\text{H}^{35}\text{Cl}$  (1-0) vibration-rotation band R(1) lines which are located at 4038.9625 and 2925.897  $\text{cm}^{-1}$ , respectively. All of the data were analyzed using a nonlinear least-squares spectral fitting procedure and a consistent set of spectroscopic line parameters. The measurements indicate a rapid increase in total HF and a more gradual increase in total HCl with both trends superimposed on short-term variability and distinct seasonal cycles with amplitudes of  $\sim 12\%$  for HF and  $\sim 7\%$  for HCl, an early spring maximum, and an early fall minimum. In the case of HF, the changes over the 13 years of measurement are sufficiently large to determine that a better fit is obtained assuming a linear increase in the total column with time than by assuming an exponential increase. For HCl, linear and exponential models fit the data equally well. Referenced to calendar year 1981.0 and assuming a sinusoidal seasonal cycle superimposed on a linear total column increase with time, HF and HCl increase rates of  $(10.9 \pm 1.1)\% \text{ yr}^{-1}$  and  $(5.1 \pm 0.7)\% \text{ yr}^{-1}$  and total columns of  $(3.17 \pm 0.11) \times 10^{14}$  and  $(1.92 \pm 0.06) \times 10^{15} \text{ molecule cm}^{-2}$ , 2 sigma, are derived, respectively; over the 13.0-year observing period, the HF and HCl total columns increased by factors of 3.2 and 1.8, respectively. The HF/HCl total columns ratio increased from a value of 0.14 in May 1977 to 0.23 in June 1990. Short-

term temporal variations in the HF and HCl total columns were found to be highly correlated; these fluctuations are believed to be caused by dynamical motions in the lower stratosphere. AER time-dependent, two-dimensional model calculations of HF and HCl total columns based on emission histories and photo-oxidation rates for the source molecules reproduce the absolute magnitudes of the HF and HCl total columns, the trends, and seasonal cycles fairly well.

The IR bands of oxygen and nitrogen have been studied based on the University of Denver and ATMOS stratospheric spectra. The IR absorption by these molecules is ideal for calibrating the line-of-sight airmasses of long-path atmospheric spectra since the strongest lines are insensitive to temperature and are moderately strong in such spectra and the volume mixing ratios of nitrogen and oxygen are constant in the atmosphere and well known. The magnetic dipole transitions in the  $^{16}\text{O}_2$  fundamental band at  $6.4\ \mu\text{m}$  have been identified for the first time, and from measurements of several isolated QR and QP lines in the stratospheric spectra, the total magnetic dipole band intensity has been derived. Accurate measurements of the positions of O- and S-branch lines of the (1,0) vibration-rotation quadrupole band of  $^{14}\text{N}_2$  have been measured and improved Dunham coefficients have been derived from a simultaneous least-squares analysis of the measurements and selected infrared and far infrared data from the literature.

In preparation for the Network for the Detection of Stratospheric Change (NDSC),  $0.002\text{-cm}^{-1}$  resolution solar and laboratory spectra recorded at the University of Denver and Mauna Loa are being analyzed. The spectra are being evaluated in terms of their signal-to-noise ratios and the reproducibility of the measurements. The better of two different interferometer systems will be selected for NDSC use at Mauna Loa based on these tests and an evaluation of the overall reliability and ease of use of the two systems.

#### Journal Publications (1990-1991)

1. Goldman, A., C. P. Rinsland, R. D. Blatherwick, and F. S. Bonomo: Spectroscopic Line Parameters for the  $\nu_6$  Band of Carbonyl Fluoride ( $\text{COF}_2$ ). Appl. Opt., **29**, 1860-1863 (1990).
2. Flaud, J.-M., C. Camy-Peyret, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith, and A. Goldman: Improved Line Parameters for Ozone Bands in the  $10\ \mu\text{m}$  Spectral Region. Appl. Opt., **29**, 1860-1863 (1990).
3. Dang-Nhu, M., R. Zander, A. Goldman, C. P. Rinsland: Identification of Magnetic Dipole Infrared Transitions of the Fundamental Band of Oxygen. J. Mol. Spectrosc., **144**, 366-373 (1990).
4. Rinsland, C. P., M. A. H. Smith, A. Goldman, V. Malathy Devi: Measurements of Lorentz Air-Broadening Coefficients and Relative Intensities in the  $\text{H}_2^{16}\text{O}$  Pure Rotational and  $\nu_2$  Bands from Long Horizontal Path Atmospheric Spectra. Appl. Opt., **30**, 1427-1438 (1991).
5. Rinsland, C. P., J. S. Levine, R. Zander, A. Goldman, N. D. Sze, M. K. W. Ko, D. W. Johnson: Infrared Measurements of HF and HCl Total Columns above Kitt Peak, 1977-1990: Seasonal Cycles, Long-Term Increases, and Comparisons with Model Calculations. J. Geophys. Res., in press (1991).
6. Rinsland, C. P., R. Zander, A. Goldman, M. R. Gunson, and C. B. Farmer: The Fundamental Quadrupole Band of  $^{14}\text{N}_2$ : Line Positions From High Resolution Stratospheric Solar Absorption Spectra. J. Mol. Spectrosc., in press (1991).
7. Camy-Peyret, C., J.-M. Flaud, A. Goldman, F. J. Murcray, R. D. Blatherwick, F. S. Bonomo, D. G. Murcray, and C. P. Rinsland: The  $\nu_4$  Band of Carbonyl Fluoride. J. Mol. Spectrosc., in press (1991).



III. MODELING AND DATA ANALYSIS

- A. STRATOSPHERIC DYNAMICS AND RELATED ANALYSIS
- B. STRATOSPHERIC CHEMISTRY, ANALYSIS AND RELATED MODELING
- C. GLOBAL CHEMICAL MODELING



A. STRATOSPHERIC DYNAMICS AND RELATED ANALYSIS

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## BIENNIAL RESEARCH SUMMARY

A. TITLE: *Assessments of Radiative Heating Near the Tropical Tropopause with Applications to Stratospheric-Tropospheric Exchange*  
(NASA Grant No. NAGW-2209)

B. INVESTIGATOR: Thomas P. Ackerman  
Department of Meteorology  
The Pennsylvania State University

### C. ABSTRACT OF RESEARCH OBJECTIVES

The research carried out under this proposal uses data acquired during the STEP-Australia field program (January-February, 1987) and a detailed radiative transfer code to study radiative flux divergence and associated heating rates in the upper troposphere and stratosphere. The objectives of the research are to:

- i) develop an understanding of the flux transfer and heating rates through the analysis of several case studies, and
- ii) use this understanding to explore the viability of mechanisms that may be important in stratospheric-tropospheric exchange.

In addition, the radiative data and model results will be used to address the impact of tropical cirrus clouds on the planetary energy budget and radiative forcing of the tropical ocean.

### D. SUMMARY OF PROGRESS AND RESULTS

Considerable progress has been made to date in the area of data analysis and simulation. The STEP data archive was obtained and read into our computer system. A computer program developed by K. N. Liou and S. Ou at the University of Utah to retrieve cloud optical depths from the 2-channel narrow-field-of-view radiometer data was obtained and converted for our needs. This program was then used to produce histograms of cirrus cloud optical depths for several of the ER-2 flights. Additional analysis of the ER-2 data was carried out to get estimates of particle size and ice water content in tropical cirrus clouds. These various data products were then combined to derive a best estimate of cirrus cloud properties for the summer monsoon period in Australia.

The estimates of cloud properties were then used as inputs into a spectrally detailed radiative transfer program. Shortwave and longwave radiative fluxes and the associated heating rates have been computed for a variety of cases. The most interesting feature of these heating rates are their large values. For optically thick cirrus, infrared heating rates at cloud base can exceed 100 K/day. Cooling rates at cloud top are slightly smaller in absolute magnitude. The implication for cirrus dynamics is that the clouds would experience relatively vigorous mixing due to radiative destabilization. This probably

contributes to the frequently-observed long lifetime of cirrus decks (greater than 10 hours) in the tropics. It also suggests that convective activity may play a role in initiating injection of tropospheric air into the lower stratosphere. Future work will focus on identifying and exploring possible mechanisms by which this can occur.

#### E. JOURNAL PUBLICATIONS

(none in this period)

# **General Circulation Modeling of Stratospheric Dynamics and Transport**

Byron A. Boville and Jeffrey T. Kiehl

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## **Research Objectives**

The objective of the proposed research is to study the dynamics of the stratosphere, the transport of trace species and the interactions between dynamics, radiation and transport. The NCAR general circulation model (GCM) of the lower and middle atmosphere (surface to upper mesosphere) will be the primary tool used in this study. A hierarchical approach will be taken to these problems. Thus, the general circulation model will be used in conjunction with parameterized chemistry to study stratospheric dynamics and the transport of relatively long lived species. A mechanistic version of the model, in which the troposphere is replaced by a specified geopotential distribution near the tropopause, will be developed and used for process studies of the impact of resolution and radiative effects on stratospheric dynamics and transport.

## **Summary of Progress**

Significant progress has been on most of the principal objectives of this proposal. The radiation parameterization has been refined to include the effects of Voigt line shapes on longwave cooling. The agreement of the longwave parameterization with line by line calculations is now excellent for the entire region from the Earth's surface to the middle mesosphere.

GCM simulations at three vertical resolutions (with level spacings of about 3km, 1.5km and 700m) have been performed to examine the effect of vertical resolution on the generation, propagation and absorption of the short vertical wave length, equatorially trapped mixed Rossby gravity waves believed to be important in forcing the QBO. It has been found that a vertical resolution of about 1 km is adequate to represent the relevant equatorial waves, but that the GCM does not generate enough wave activity at any vertical resolution to generate a QBO. Results of the high vertical resolution integrations have been as a guide to identify a new class of planetary scale Rossby-gravity waves in satellite observations of the upper stratosphere.

A mechanistic model of the stratosphere has been developed and applied to several stratospheric problems. The model has been used to produce the first three-dimensional numerical simulations of the quasi-biennial oscillation (QBO) of the equatorial lower stratosphere. The sensitivity of the QBO simulations to the wave forcing amplitude, the horizontal and vertical resolution of the model, and the inclusion of the annual cycle of radiative driving and extratropical planetary wave forcing has been studied. The mechanistic model has also been used to study the evolution of the polar vortex with specified forcing and varying horizontal resolution and radiative driving.

Two long lived trace constituents ( $\text{N}_2\text{O}$  and  $\text{CH}_4$ ) have introduced into the GCM in collaboration with other scientists (R.R. Garcia, F. Sassi, J.R. Holton, and P. Mote).  $\text{N}_2\text{O}$  is treated as a purely passive tracer with a tropospheric source and stratospheric sink, while the sink of  $\text{CH}_4$  is used to form  $\text{H}_2\text{O}$  which affects the radiative cooling in the upper stratosphere. The sink of both constituents is parameterized through specified lifetimes determined from two-dimensional model calculations.

#### **Journal Publications, 1990–1991**

- Boville, B. A., and W. J. Randel, 1991: Equatorial waves in a stratospheric GCM: Effects of vertical resolution. *J. Atmos. Sci.*, accepted.
- Kiehl, J. T., and B. P. Briegleb, 1991: A new parameterization of the absorptance due to the  $15\text{-}\mu\text{m}$  band system of carbon dioxide. *J. Geophys. Res.*, **96**, 9013–9019.
- Randel, W. J., B. A. Boville and J. C. Gille, 1990: Observations of planetary mixed Rossby-gravity waves in the upper stratosphere. *J. Atmos. Sci.*, **47**, 3092–3099.
- Takahashi, M., and B. A. Boville, 1991: A three-dimensional simulation of the equatorial quasi-biennial oscillation. *J. Atmos. Sci.*, accepted.

**Studies of Dynamical Processes  
Affecting the Distribution of Stratospheric Ozone**

Principal Investigator: Kenneth P. Bowman  
Department of Atmospheric Sciences  
University of Illinois at Urbana-Champaign

**Research Objectives**

The purpose of this research is to understand large-scale ozone transport processes in the stratosphere. Observational and modeling studies are used to investigate the global quasi-biennial oscillation patterns in total ozone, and ozone transport during the breakdown of the Antarctic polar vortex. The observational methods being used are statistical and dynamical analyses of Nimbus 7 Total Ozone Mapping Spectrometer (TOMS) data and conventional meteorological observations (Randel, 1987). The lag-correlation technique developed by Bowman (1989) is being used to identify quasi-biennial variations in tropical and extratropical dynamical fields, including extratropical stationary waves. The same data sets will be used to study the relationship between waves in the ozone and dynamical fields during the Antarctic spring, when rapid ozone transport marks the end of the ozone hole. A global equivalent-barotropic numerical model developed by O'Sullivan and Salby (1989) is being used to study reversible and irreversible ozone transport during that period.

**Progress and Results**

This project is entering the second year of a planned three year study. Progress on the major thrusts of the research are discussed below.

- 1) Observational studies. Analysis of TOMS ozone data shows that ozone transport by planetary-scale waves in the Antarctic stratosphere is almost completely reversible during the early spring season. Ozone is transported poleward as wave amplitudes increase and equatorward as they decrease. The filling of the ozone hole later in the spring is not associated with especially large wave amplitudes, and, in fact, often occurs as wave amplitudes are decreasing, when ozone transport is normally equatorward (Bowman, 1990).

Global monthly-mean geopotential height, temperature, and linear-balanced zonal wind fields have been calculated from Randel's data set. In order to determine the global structure of the QBO, the dynamical variables have been correlated at different lags with observed monthly-mean zonal winds at Singapore, which are driven almost solely by the equatorial QBO. Early results show a significant correlation pattern between the Singapore winds at 20 mb and geopotential heights in middle and high latitudes throughout the

stratosphere and into the troposphere similar to those found by Bowman (1990) in the TOMS total ozone data.

- 2) Modeling studies. Numerical simulations of the breakdown of the Antarctic circumpolar vortex are being carried out with equivalent-barotropic model using observed monthly-mean wind profiles from Randel's data set. Forcing amplitudes and spatial structures are also developed from the observations. Initial experiments show a strong sensitivity to the amplitude of the forcing, and weak sensitivity to radiative damping timescales. Tracer experiments to investigate the transport of ozone into and out of the Antarctic polar vortex are now beginning.
- 3) Methods for the design and analysis of numerical experiments. An additional area of study that has arisen in the course of this research involves methods for efficiently conducting numerical experiments. In collaboration with Dr. Jerome Sacks of the Department of Statistics at the University of Illinois, we have developed and tested methods for the design and analysis of numerical experiments with the shallow water model that are especially useful in multi-dimensional parameter spaces. The analysis method fits a statistical model to the output of the numerical model. The statistical model provides estimates of the uncertainty of predicted numerical model output, which can provide guidance on where in the parameter space to conduct further experiments. These methods can provide major improvements in the efficiency with which numerical experiments are conducted and can result in a major improvement in the utilization of computational resources. (Paper in preparation.)

## **Publications**

Bowman, Kenneth P., 1990. Evolution of the the Total Ozone Field during the Breakdown of the Antarctic Circumpolar Vortex, *J. Geophys. Res.*, **95**, 16,529–16,543.

Bowman, Kenneth P., Jerome Sacks, and Yue-Fang Chang, On the Design and Analysis of Numerical Experiments, *in prep.*

A) Title: SME Temperature Studies of the Mesosphere and Upper Stratosphere

B) Investigators: R. Todd Clancy and David W. Rusch  
Laboratory for Atmosphere and Space Physics  
University of Colorado  
Boulder, CO 80309

C) Abstract of Proposed Research:

We propose to extend Solar Mesospheric Explorer (SME) measurements of atmospheric temperatures over the 40-60 km altitude region. This involves analysis of SME visible and longer wavelength ultraviolet limb radiance profiles. These upper stratospheric/lower mesospheric temperature observations will be combined with previous SME mesospheric temperatures to provide 40-90 km global atmospheric temperature profiles over the 1982-1986 period. A wide range of studies based on these temperatures include 1982-1986 temperature trends and a combined analysis of stratospheric and mesospheric semi-annual oscillations (SAO) in equatorial atmospheric temperatures.

D) Summary of Progress:

We have analyzed the SME visible limb radiances to derive monthly average upper stratospheric temperatures (40-55 km) over the 1982-1986 period. We have also inverted the SME longer wavelength (300-313 nm) ultraviolet limb radiances to calculate 1983-1986 lower mesospheric (50-80 km) temperatures. These temperatures provide continuity between the upper mesospheric temperatures previously derived (Clancy and Rusch, 1989) and the new upper stratospheric SME temperatures from the visible SME limb profiles. As a result, we now have a 1982-1986 global data set of upper stratospheric/mesospheric temperatures of unprecedented vertical resolution (4 km). We have begun to analyze the stratopause SAO with the new visible temperature data set. We have also constructed a comparison between NMC and SME temperatures in the upper stratosphere.

E) Journal Publications:

Clancy, R.T. and D.W. Rusch, Solar Mesospheric Explorer temperature climatology of the mesosphere as compared to the CIRA model, *CIRA: 1986. Part II - Middle Atmosphere Models*, ed. M. Roemer, J.J. Barnett and K. Labitake, *Ad. Space Res.*, **10**, 187-206, 1990.

Garcia, R.R. and R.T. Clancy, Seasonal variation in equatorial mesospheric temperatures observed by SME, *J. Atmos. Sci.*, **47**, 1666-1673, 1990.

## A. Dynamical Meteorology of the Equatorial and Extratropical Stratosphere

### B. INVESTIGATORS:

*Timothy J. Dunkerton, Principal Investigator*

*Donald P. Delisi*

*Mark P. Baldwin*

*Francis X. Crum*

*Northwest Research Associates, P.O. Box 3027, Bellevue, WA 98009*

### C. RESEARCH OBJECTIVES

The project is an observational and theoretical study of large-scale waves, mean flow oscillations, interannual variability and trends in the middle atmosphere. Upper air, rocketsonde, and satellite data were used to elucidate the climatological behavior of equatorial waves, quasi-biennial and semiannual oscillations, and extratropical wintertime flow. Theoretical models were utilized to study the mean meridional circulation of the middle atmosphere and perturbations due to tropical heating, extratropical wave drag, equatorial waves and inertial instability.

### D. PROGRESS SUMMARY

Fifteen years of upper air rawinsonde data from near-equatorial stations were examined for evidence of Rossby-gravity and Kelvin waves and their modulation by the QBO and seasonal cycle. It was shown that large seasonal variations of 3-6 day meridional velocity power exist in the upper troposphere and lower stratosphere. The lower stratospheric variation of wave activity over the Maritime continent was consistent with seasonal modulation of QBO east phase onsets; evidence from other tropical areas was less conclusive and requires further study. Twenty years of rocketsonde data from tropical and Northern hemisphere subtropical and midlatitude locations allowed us to construct a climatology of quasi-biennial and semiannual oscillations, 0-84 km, and to investigate trends in the middle atmosphere. There was clear evidence of SAO modulation by the QBO, along with seasonal modulation of the QBO (breakdown into approximate biennial and triennial cycles, though not exact synchronization). Decadal variation and a downward trend of upper stratospheric temperature were also evident; the former was positively correlated with solar cycle and most pronounced in early NH winter, extending to the midlatitude winter jet. Warming due to El Chichón in 1982 was accompanied by large cooling in the tropical upper stratosphere; model simulations suggest that tropical heating was only partly responsible for the cooling, with likely influence from SH midlatitude wave event and warming.

Twenty-eight years of extratropical NH data revealed quasi-biennial variations of mean circulation and planetary wave fluxes, linear correlation with solar cycle, and nonlinear



modulation term (late winter only). There was indication of QBO signal in recent SH data in subtropical latitudes, possibly associated with the NH QBO signal, as it was primarily evident in NH winter.

Modeling studies of mean meridional circulation established the hybrid nature of circulation driven by tropical thermal heating and midlatitude body forces. The role of meridional circulation in the QBO and SAO was studied showing how the period of the QBO depends on extratropical body forces and requires larger equatorial wave fluxes than observed. Theory of equatorial wave excitation was examined in the context of nonlinear CISK models. Excitation of equatorial waves and inertial instabilities is currently of interest in middle atmosphere GCMs.

#### E. JOURNAL PUBLICATIONS

- Dunkerton, T.J., 1990: Annual variation of deseasonalized mean flow acceleration in the equatorial lower stratosphere. *J. Meteor. Soc. Japan*, *68*, 499-508.
- , and M.P. Baldwin, 1990: Quasi-biennial modulation of planetary wave fluxes in the Northern hemisphere winter. *J. Atmos. Sci.*, *48*, 1043-1061.
- , 1990: LIMS observation of traveling planetary waves and potential vorticity advection in the stratosphere and mesosphere. *J. Geophys. Res.*, *96*, 2813-2834.
- , and D.P. Delisi, 1991: Anomalous temperature and zonal wind in the tropical upper stratosphere, 1982/83. *J. Geophys. Res.*, in press.
- , and F.X. Crum, 1991: Scale selection and propagation of wave-CISK with conditional heating. *J. Meteor. Soc. Japan*, in press.
- Baldwin, M.P., and T.J. Dunkerton: Quasi-biennial oscillation above 10 mb. *Geophys. Res. Lett.*, *18*, 1205-1208.
- Dunkerton, T.J., 1991: Intensity variation and coherence of 3-6 day equatorial waves. *Geophys. Res. Lett.*, in press.
- Crum, F.X., and T.J. Dunkerton, 1991: Analytic and numerical models of wave-CISK with conditional heating. *J. Atmos. Sci.*, submitted.
- Dunkerton, T.J., and M.P. Baldwin, 1991: Modes of interannual variability in the stratosphere. *Geophys. Res. Lett.*, submitted.

## Research Summary 1990-1991

### Studies of Middle Atmospheric Processes using Satellite Data and Models

Investigators: J. C. Gille and W.J. Randel  
National Center for Atmospheric Research

#### Research Objectives:

The studies undertaken here seek to improve fundamental knowledge of global scale dynamical and chemical processes in the middle atmosphere, based upon analyses of satellite data. Research has focused on analyses of midlatitude and equatorially-trapped waves in the stratosphere, and their observed effects on constituent transport and photochemistry.

#### Summary of Progress:

Several observational studies of equatorially-trapped waves have been completed, prompted by results from a very high vertical resolution (0.7 km) version of the NCAR Community Climate Model (CCM1) over 0-80 km. A study of observed equatorial waves in the upper troposphere based on ECMWF data was made to validate the tropospheric forcing in CCM1. Using LIMS data, we have presented the first observational evidence of planetary mixed Rossby-gravity waves in the upper stratosphere. LIMS data was also used to identify and quantify stratospheric constituent ( $O_3$ ,  $H_2O$ ,  $HNO_3$  and  $NO_2$ ) waves associated with Kelvin modes. Based on these results, we used eight years of SBUV ozone measurements to monitor long term variability of Kelvin waves in the stratosphere, finding strong modulation by the semiannual zonal wind oscillation (SAO). We have also identified Rossby normal mode oscillations in the global ozone field; both these and Kelvin waves provide examples of linear wave behavior in the real atmosphere, allowing detailed comparisons of observed transport and photochemistry with linear wave theory.

LIMS temperature data were used to develop the first global climatology of gravity wave variance in the middle atmosphere, as a function of latitude, altitude and season. Furthermore, these studies showed spatial and temporal correlations between gravity wave variance and independently determined residuals in the zonal momentum balance, indicating that gravity waves are responsible for the inferred drag.

We have calculated horizontal winds from stratospheric brightness temperature data, gridded via the fast Fourier synoptic mapping technique of Salby, to study the dynamics of the '4-day' wave in the SH polar stratosphere. Results show clear evidence for a dynamic instability source mechanism, with the source related to the 'double jet' structure observed in the upper stratosphere - mesosphere. These asynoptically mapped data and derived circulation statistics were also compared with those from standard NMC stratospheric Cressman analyses, allowing direct evaluation of the two mapping schemes for the situation where much of the variance is due to high frequency transients.

### Journal Publications 1990-1991:

- Randel, W.J., 1990: Kelvin Wave Induced Trace Constituent Oscillations in the Equatorial Stratosphere. *J. Geophys. Res.*, 95, 18,641-18,652.
- Randel, W.J., B.A. Boville and J.C. Gille, 1990: Observations of Planetary Mixed Rossby-Gravity Waves in the Upper Stratosphere. *J. Atmos. Sci.*, 47, 3078-3091.
- Fetzer, E.J., 1990: A global climatology of middle atmosphere inertio-gravity waves. Ph. D. Thesis, University of Colorado, 269 pp.
- Randel, W.J., and I.M. Held, 1991: Phase Speed Spectra of Transient Eddy Fluxes and Critical Layer Absorption. *J. Atmos. Sci.*, 48, 688-697.
- Hirota, I., M. Shiotani, T. Sakurai, and J. C. Gille, 1991: Kelvin waves near the equatorial stratopause as seen in SBUV ozone data. *J. Meteor. Soc. Japan*, 69,179-186.
- Randel, W.J., and L. R. Lait, 1991: Dynamics of the 4-day wave in the Southern Hemisphere winter stratosphere. *J. Atmos. Sci.*, in press.
- Randel, W.J., and J.C. Gille, 1991: Kelvin wave variability in the upper stratosphere observed in SBUV ozone data. *J. Atmos. Sci.*, in press.
- Randel, W.J., 1991: Upper tropospheric equatorial waves in ECMWF analyses. *Quart. J. Roy. Meteor. Soc.*, accepted.
- Boville, B.A., and W.J. Randel, 1991: Equatorial waves in a stratospheric GCM: Effects of vertical resolution. *J. Atmos. Sci.*, accepted.
- Fetzer, E.J., and J.C. Gille, 1991: Gravity wave variance in LIMS temperatures. Part I: Variability and comparison with background winds. *J. Atmos. Sci.*, submitted.
- Fetzer, E.J., and J. C. Gille, 1991: Gravity wave variance in LIMS temperatures. Part II: Comparison with the zonal mean momentum balance. In preparation.
- Randel, W.J., 1991: Global normal mode Rossby waves observed in stratospheric ozone data. In preparation.

## BIENNIAL RESEARCH SUMMARY

### A. Dynamical Investigations of the Middle Atmosphere with a 2-D Model

#### B. Dr. Matthew H. Hitchman, Principal Investigator

Department of Meteorology, University of Wisconsin - Madison

Dr. Guy Brasseur, Co-Investigator

National Center for Atmospheric Research

C. The fundamental goal is to improve our understanding of dynamics and tracer transport in the middle atmosphere through the use of a two dimensional numerical model. The model contains approximately 50 trace species, a detailed radiative code, and has fully interactive zonal mean and wave dynamics, including a new method of closure for the effects of planetary scale Rossby waves. Three areas of study are emphasized for the period 1990-1991: 1) completing sensitivity studies of this new Rossby wave parameterization, 2) the equatorial semiannual and quasibiennial (QBO) oscillations, and 3) systematically assessing the relative roles of annual insulation variation and wave driving by gravity, Rossby, and Kelvin waves in establishing the observed basic state.

D. In studying the effects of wave driving in a 2D model where the temperature equation is explicitly integrated and the zonal wind is solved by a balance relation, we have found that the circulation is not as responsive as it ought to be, especially in the tropics. We have therefore undertaken to solve the zonal momentum equation in addition, with better results in the tropics. In calculating the effects of Rossby waves, a wave activity conservation equation is solved, where a radiative damping coefficient is specified. We now implement a damping coefficient that includes mechanical dissipation due to the wave breaking process. Mr. William Sea will complete his Master's thesis this December, entitled *A Modeling Study of Rossby Wave Activity in the Middle Atmosphere*, and we are writing a paper on the subject.

Mr. Kenneth Bywaters completed his Master's Degree in October 1990, entitled *Lower Stratospheric Gravity Waves Observed by the Jicamarca MST Radar*. This work enhances our understanding of equatorial middle atmosphere dynamics and how to parameterize gravity wave effects in our 2D model. Although not included in the original research objectives, Jicamarca data analysis supported by NASA has contributed to the first two publications listed below.

Mr. Charles Trepte is a Ph.D. candidate working on the relationship between the stratospheric aerosol layer, the QBO, and the distribution of potential vorticity. In addition to using the 2D model, Trepte is analyzing SAGE-II aerosol and ozone data. We have found a remarkable confinement of aerosol in a tropical vault associated with the QBO. Lofting occurs in a high plume over the equator during the easterly phase of the QBO, with a double

'rabbit ear' structure during the westerly phase. Tracers that enter the stratosphere via the tropical tropopause undergo a two-step process: mixing in the equatorial vault, followed by detrainment governed by the QBO and wintertime Rossby wave ventilation. This work has led to the third publication listed below and we are writing a longer paper on the relationship among aerosols, ozone, potential vorticity, and Rossby wave transport.

We have used the 2D model to calculate radiative equilibrium distributions of all quantities interactively, and systematically estimated departures therefrom due to the annual cycle, the radiative circulation, eddy diffusion, the upward extension of the tropospheric circulation, inertial instability, gravity wave driving, and Rossby wave driving. One new result is that the summer polar lower stratosphere is not in radiative equilibrium.

The aerosol QBO, radiative equilibrium, and Jicamarca radar work were each reported at the IAMAP meeting in Vienna in August 1991. Finally, I have used the 2D model as an educational tool in Meteorology 605, The Middle Atmosphere, which was run via MacIntoshes and a SPARCStation acquired under this grant. Several students' projects led to improvements or better understanding of the model.

#### E. Publications

- 1) Hitchman, M. H., K. W. Bywaters, D. C. Fritts, L. Coy, E. Kudeki, F. Surucu, 1991: Ten day mean winds and momentum fluxes in the stratosphere and mesosphere over Jicamarca, Peru during June and August 1987. *J. Atmos. Sci.*, *in press*.
- 2) Fritts, D. C., L. Yuan, M. H. Hitchman, L. Coy, E. Kudeki, and R. F. Woodman, 1991: Dynamics of the equatorial mesosphere observed using the Jicamarca MST radar during June and August 1987. *J. Atmos. Sci.*, *in press*.
- 3) Trepte, C. R. and M. H. Hitchman, 1991: Tropical stratospheric circulation diagnosed in satellite aerosol data. *Nature*, *in review*.

## **Report to NASA Upper Atmosphere Research Program**

### **Research Summary for 1990- 1991**

**TITLE:** Wave Dynamics and Transport in the Stratosphere

**PRINCIPAL INVESTIGATOR:** Professor J. R. Holton, University of Washington

**ABSTRACT:** This grant supports a program of theoretical studies, numerical modeling, and data analysis designed to elucidate the dynamics of motions in the stratosphere and their role in the transport of heat, momentum, and trace chemical substances in the lower stratosphere, and across the tropopause. The emphasis of the project is on the physics of wave motions and the role of wave, mean-flow interactions in maintaining the observed heat, momentum, and trace species budgets.

#### **SUMMARY OF PROGRESS 1989 - 1990**

i) Much of the work during the past year has involved use of a two-dimensional nonhydrostatic model for cumulonimbus convection to simulate convectively generated gravity waves in the lower stratosphere. We have found that severe midlatitude squall lines can produce gravity waves, which appear to have the potential for playing a significant role in the momentum budget of the lower stratosphere, and may also be important for mixing of tracers. This work has been submitted for publication.

ii) Simulation of the equatorial semiannual oscillation of the  $\text{N}_2\text{O}$  distribution in the stratosphere: Graduate student Woo-kap Choi has utilized a two-dimensional tracer model, based on an isentropic coordinate formulation, to examine the annual and semiannual variations in  $\text{N}_2\text{O}$ . He finds that the observed large amplitude semiannual oscillation in  $\text{N}_2\text{O}$  can be simulated only if the semiannually varying component of the mean vertical velocity in the equatorial region is much larger than estimated in previous studies based on theoretical radiative heating-cooling calculations. His numbers can be supported if it is assumed that current satellite instruments underestimate the magnitude of temperature variations in the equatorial stratosphere, which is certainly plausible given the rather poor vertical resolution of the satellite data. His work is contained in a PhD thesis submitted in June 1990, and has been accepted subject to revision in the *Journal of the Atmospheric Sciences*.

iii) Postdoctoral Research Associate Dr. John Austin developed a photochemical-transport model that employs an Eulerian grid with latitude and longitude coordinates on a single isentropic surface, specified to be near 850 K. There are 40 species and 107 reactions in the model, the equations for which are solved explicitly with an algorithm that fully accounts for diurnal variations. Species are advected implicitly using a semi-Lagrangian technique in which 12 hour air particle trajectories are computed and then reinitialized back onto the Eulerian grid. The model utilizes wind and temperature fields supplied from a three dimensional dynamical model integration designed to simulate a sudden warming. The photochemical model was integrated for 12 days of an idealized wavenumber one disturbance. The results for the long-lived model tracers such as  $\text{N}_2\text{O}$  show excellent correlation with the potential vorticity distribution, providing confidence in the transport scheme. The distribution of the tracers and the nighttime distribution of the reservoir species show the effect of the wave disturbance in enhancing gradients at the edge of the vortex region and in low to mid-latitudes where a tongue of low potential vorticity air is advected. For the radical species, the differences in the steepness of the gradients at the nighttime terminator and the daytime terminator are clearly apparent. The details of other aspects of the diurnal variation are also seen in the results. The model provides an interesting way of viewing the full complexity of the photochemistry in the presence of large scale advection and could be used to study dynamical-chemical interactions in the real atmosphere. This

work has been published in the *Journal of Geophysical Research* (Austin and Holton, 1989).

iv) In the extratropics the time and zonal mean air mass exchange across an isobaric surface in the stratosphere depends primarily on the rate of eddy dissipation in the first few scale heights above that level. Since in the lower and middle extratropical stratosphere the eddy dissipation is primarily due to dissipating planetary and synoptic scale eddies, it is possible to utilize conventional climatological data to estimate the mean downward mass flow across the 100 mb surface in the extratropics in each hemisphere. The compensating upward mass flow across the 100 mb level in the tropics (effectively the tropical tropopause) can then be estimated by mass continuity. A first attempt to utilize this scheme to estimate seasonal and annual exchange rates using readily available data was completed by the PI and published in the *Journal of the Atmospheric Sciences*.

#### JOURNAL PUBLICATIONS 1990- 1991

Holton, J. R. (1990) On the global Exchange of Mass between the stratosphere and troposphere. *J. Atmos. Sci.*, **47**, 392-395.

Austin, J., and J. R. Holton (1990) A model of stratospheric chemistry and transport on an isentropic surface. *J. Geophys. Res.*, **95**, 11,875-11,900.

Austin, J., R. L. Jones, D. S. McKenna, A. T. Buckland, J. G. Anderson, D. W. Fahey, C. B. Farmer, L. E. Heidt, M. H. Proffitt, A. F. Tuck, and J. F. Vedder (1990:) Lagrangian Photochemical Modeling Studies of the 1987 Antarctic Spring Vortex 2. Seasonal Trends in Ozone. *J. Geophys., Res.*, **94**, 16,717-16,735.

Choi, Woo Kap , and J. R. Holton (1991) : Transport of N<sub>2</sub>O in the stratosphere related to the equatorial semiannual oscillation. *J. Atmos. Sci.*, **48** (submitted for publication)

Fovell, R. , D. Durran, and J. R. Holton, 1991: Numerical simulations of convectively generated gravity waves in the stratosphere. *J. Atmos. Sci.*, **48** (submitted for publication)

## **Biennial Research Summary, NASA Upper Atmosphere Research Program**

**A. Title of Research Task:** Transport and Circulation of the Middle Atmosphere: Mixing of the Polar Vortex.

**B. Investigator and Institution:** Conway B. Leovy, Department of Atmospheric Sciences, AK-40, University of Washington, Seattle, WA 98195.

**C. Abstract of Research Objectives:** This research task is aimed at improving our understanding of processes responsible for vertical and horizontal mixing of potential vorticity and trace gases in the middle atmosphere using diagnosis of global data sets and modeling. Emphasis is on mixing processes in the vicinity of polar stratospheric vortices. One hypothesis under investigation is that differential vertical motion associated with stratospheric warmings followed by lateral displacement and subsequent vertical mixing by small scale processes (turbulence, gravity waves) plays an important role in mixing near the polar vortex.

**D. Summary of Progress and Results:** A key component of this investigation is accurate determination of heating rates from which cross-isentropic transport can be deduced. Graduate student Von Walden completed construction and validation of an accurate and efficient algorithm for calculating heating rate in the polar stratosphere due to CO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O, and aerosols, and has applied it to the southern hemisphere stratospheric polar vortex for both undisturbed and disturbed (ozone hole) conditions. An important factor controlling whether vertical velocity is upward or downward in the disturbed polar vortex is the effective surface emission temperature (due to clouds or the snow surface). This work constituted Walden's M.S. thesis; he has elected to move to another project for his Ph.D. thesis, and further work on the project awaits the arrival of a new graduate student in Autumn 1991.

Visiting Scientist Rashid Akmaev (University of Leningrad) focused his efforts on quite a different topic, circulation and transport in the mesosphere. He completed and tested a mesospheric general circulation model which extends from 15 to 150 km and incorporates the effects of non-local thermodynamic equilibrium and gravity wave transports of heat and momentum. The model sensitivities to gravity wave properties and the distribution of gravity waves near the tropopause were tested, and results were compared with mesospheric observations of gravity waves from a variety of sources. The results showed that the model can be a useful tool for diagnosing gravity wave fluxes, as well as investigating other mesospheric dynamical and physical problems such as the role of energy exchange processes on non-LTE heating rates near the mesopause. This research is currently in press (JATP), and we are exploring mechanisms for possible longer term collaboration between the University of Washington and the University of Leningrad group.

**E. Journal Publications:**

Sun, C.-R., and C.B. Leovy, 1990. Ozone variability in the equatorial middle atmosphere. J. Geophys. Res., **95**, 13,829-13,849.



Akmaev, R.A. & V.I. Fomichev, 1991. A method for adaptation of a matrix type parameterization of atmospheric radiative cooling for an arbitrary vertical coordinate grid. J. Atmos. Terr. Phys. (in press).

Akmaev, R.A., V.I. Fomichev, N.M. Gavrilov, & G.M. Shved, 1991. Simulation of the zonal mean climatology of the middle atmosphere with a three-dimensional spectral model for solstice and equinox conditions. J. Atmos. Terr. Phys. (in press).

## **Biennial Research Summary, NASA Upper Atmosphere Research Program**

A. Title of Research Task: Transport and Circulation of the Middle Atmosphere: Tides in the Middle Atmosphere.

B. Investigator and Institution: Conway B. Leovy, Department of Atmospheric Sciences, AK-40. University of Washington, Seattle, WA 98195.

C. Abstract of Research Objectives: This research task is to utilize data from the Nimbus 7 Limb Infrared Monitor of the Stratosphere (LIMS) together with models to diagnose the tidal fields in the stratosphere and lower mesosphere between 20 and 60 km. We are particularly interested in diagnosing the non-migrating components of the diurnal tide that are forced by land sea variations in heating.

D. Summary of Progress and Results: Graduate student Ruth Lieberman has completed and published her analysis of the diurnal non-migrating tidal components based on the LIMS data (Lieberman, 1991). Since a polar orbiting satellite can generally reveal only the wave number zero and eastward propagating components of the non-migrating diurnal tide, inferences of tidal physical processes from these data require additional research. We have chosen to complete the picture of the non-migrating tides by combining the LIMS data analysis with a theoretical calculation using linear tidal theory. What is required to do this is the distribution of thermal forcing due to the non-migrating diurnal components of the heating field, in particular the fields of latent and convective heating. To obtain estimates of these, Lieberman has carried out one run of the NCAR Community Climate Model (CCM1) and two runs of the improved version of the model (CCM2, for January and July conditions, in collaboration with Byron Boville and his colleagues at NCAR. To the extent possible, Lieberman is validating the diurnal heating fields against observations, although the observational data base permits only limited validations. This comparison effort is now nearly complete, and Lieberman is also working on development of the computational algorithm needed to calculate the non-migrating components of the diurnal tide, given knowledge of the thermal forcing. When this task is completed, comparison of the LIMS signatures of non-migrating tidal components with the theoretical model should be possible, and will lead to improved understanding of diurnal variations in the middle atmosphere.

This work is proceeding in accordance with our original schedule, and Lieberman expects to complete all of these tasks and her Ph.D. thesis by early spring 1992.

E. Journal Publications:

Lieberman, Ruth S., 1991. Nonmigrating diurnal tides in the equatorial middle atmosphere. J. Atmos. Sci., 48, 1114-1123.

# General Circulation of the Southern Hemisphere Stratosphere

Principal Investigators: Carlos R. Mechoso  
Collaborators: John D. Farrara and Gloria L. Manney  
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## Research Objectives

The goal of this project is to better understand the dynamical processes at work during the seasonal evolution of the Southern Hemisphere (SH) stratosphere and the reasons for the observed interhemispheric differences in the stratospheric circulation. The methodology for research is based on two complementary lines of investigation. One uses observational data and aims to provide a three-dimensional view of the stratospheric circulation. The other uses three-dimensional, primitive-equation numerical models of the atmosphere to test hypotheses arising from the analysis of observational data.

## Summary of Progress and Results

A detailed observational study of the behavior of the zonal wavenumber two component of the flow (wave 2) in the southern hemisphere stratosphere was performed. Wave 2 is characterized by a broad meridional structure with peak amplitudes between 55 and 65°S and regular eastward propagation. Largest wave 2 amplitudes are generally seen in late winter (August/September). There is considerable interannual variability in the speed of eastward propagation with periods ranging from 5 to 40 days.

Examination of the vertical structure of wave 2 shows two distinct patterns. Episodes of largest wave 2 growth involve all levels above the middle troposphere and appear associated with upward propagation of wave energy. Several episodes of weaker wave 2 growth are confined to the stratosphere. Several mechanisms are possible for the growth of wave 2 during these episodes including in-situ instability and nonlinear wave-wave interactions.

During several of the episodes of where wave 2 growth is confined to the stratosphere, wave 2 momentum fluxes are equatorward in a region on the equatorward side of the westerly wind maximum, consistent with a transfer of kinetic energy from the zonal mean flow to wave 2. The conditions for quasi-geostrophic instability are frequently satisfied during these periods. Moreover, the structure of wave 2 during these episodes shows characteristics similar to modes obtained in idealized studies of barotropic instability. In view of these facts, we analyzed the stability of the stratospheric flow for the episodes when wave 2 growth is confined to the stratosphere using several linear models of quasi-geostrophic instability.

Each of the models gives unstable modes for several zonal wavenumbers. In the simplest model, the barotropic model with zonally symmetric basic flow, wave 3 is usually most unstable. In the models with more realistic basic flows, including either vertical structure or zonal asymmetry, wave 2 is usually the most unstable wave. The similarities between model results and observations during episodes when wave 2 growth appears confined to the stratosphere suggests that instability may be an important mechanism for wave 2 growth at those times.

A multi-level analysis of the low-frequency variability of the southern hemisphere winter circulation was completed. The variability was studied using multi-level geopotential height data for nine winters (1979-1987). Empirical orthogonal function (EOF) analysis was applied at five levels in the stratosphere (70, 30, 10, 5 and 2 mb) and five levels in the troposphere (700, 500, 300, 200 and 100 mb) to obtain a statistical description of this variability.

For the stratosphere, the EOF analysis yielded five distinct structures which fall into two classes. The first three EOFs at all levels form the first class. This class represents anomalies that are dominated by zonal wavenumber one, exhibit a westward tilt with height and travel slowly eastward in their developing stage and are equivalent barotropic in their decaying stage. These anomalies tend to develop in early winter. The fourth and fifth EOFs form the other class. This class represents anomalies that are dominated by wavenumber two, and tilt noticeably, but less strongly than the first class, westward with height. These anomalies tend to develop in late winter and travel eastward more rapidly than those of the first class.

For the troposphere, EOFs at different levels have comparable amplitude and nearly identical phase. Three (the first, third and fourth) of our four leading EOFs correspond to composites of quasi-stationary events in the southern hemisphere middle troposphere. There are no apparent systematic relationships between the time variations in these four tropospheric structures and those of the five structures identified in the stratosphere.

A southern hemispheric counterpart of the early winter Canadian warming in the northern hemisphere was discovered. The flow in the southern hemisphere during early winter can become highly disturbed. The strong early-winter disturbances originate over the South Pacific and decay over the South Atlantic. The stratospheric flow during disturbed early winters has several features in common with that during Canadian warmings in the northern hemisphere.

During southern hemisphere episodes, the circulation is dominated by a large, slowly eastward moving disturbance with a wave 1 pattern. The disturbances are nearly equivalent barotropic and have largest amplitudes in the lower and middle stratosphere. Further, temperature increases associated with the development of the disturbance, both locally and in the zonal mean, are smaller than those observed during final warmings in the southern hemisphere and major warmings in the northern hemisphere.

Inspection of isentropic potential vorticity maps during the development of these disturbances show several distinctive features. There is a bifurcation of the westerly jet around a region where irreversible buckling of contours of potential vorticity ( $Q$ ) occurs. This buckling region is well away from the zero-wind line. Despite the strong irreversible buckling of isopleths of  $Q$  and the mixing of  $Q$  possibly associated with it, there is no sign of the formation of a main vortex/surf zone in the average distribution of  $Q$ .

Hypothesis-testing simulations with the SMM suggest that the development of the early-winter stratospheric disturbances is connected with the amplification of wave 1 at 100 mb. In addition, they suggest that the development of stratospheric disturbances is relatively insensitive to the structure of the zonal mean flow in the stratosphere and the phase speed of the disturbance.

### Journal Publications

- Mechoso, C. R., 1990: The final warming of the stratosphere. In *Dynamics, Transport and Photochemistry in the Middle Atmosphere of the Southern Hemisphere*, A. O'Neill, Ed., Kluwer Academic Publishers, P. O. Box 17, 330 AA Dordrecht, The Netherlands.
- Manney, G. L., J. D. Farrara and C. R. Mechoso, 1991: The behavior of wave 2 in the southern hemisphere stratosphere during late winter and early spring. *J. Atmos. Sci.*, **48**, 976-998.
- Mechoso, C. R., J. D. Farrara and M. Ghil, 1991: Intraseasonal variability of the winter circulation in the southern hemisphere atmosphere. *J. Atmos. Sci.*, **48**, 1387-1404.
- Manney, G. L., C. R. Mechoso, L. S. Elson and J. D. Farrara, 1991: Planetary scale waves in the southern hemisphere winter stratosphere: Stability analysis. *J. Atmos. Sci.*, in press.
- Farrara, J. D., M. Fisher, C. R. Mechoso and A. O'Neill, 1991: The southern stratosphere in early winter. Submitted to *J. Atmos. Sci.*

A. Title of Research Task:

**Upper Atmosphere Dynamics**

B. Investigators and Institutions:

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C. Research Objectives:

The spatial distribution of stratospheric ozone is useful in diagnosis of some features of the large-scale atmospheric circulation, and the ozone may also interact with the atmospheric general circulation. Local maxima in the column ozone distribution are often associated with disturbances in the lower stratosphere and upper troposphere. One research objective is to explore these issues by means of time series analysis of a zonal index of total column ozone, to suggest the existence or nonexistence of relationships between column ozone and dynamical processes which are known to occur on various time scales. Another objective is to investigate intraseasonal variability at the equator using column ozone data and stratospheric temperatures. The source of data for these studies is the Total Ozone Mapping Spectrometer (TOMS) and the Microwave Sounding Unit (MSU) channel 4 data for the period 1979-1988.

D. 1990 and 1991 Accomplishments:

The midlatitude ozone index, defined to be the difference between the zonally averaged column ozone in a high latitude minus that for a low latitude, has been computed for the 7-year period 1981-1987 for the Northern and Southern Hemispheres. An ozone index for the North Atlantic region (100W to 20E) has also been computed, as well as an equatorial zonal average ozone column. Power spectra have been constructed from the above time series to determine the peaks that are significant above red noise. The more significant peaks are associated with the 6-month and longer periods and with a 10- to 15-day period. The time domain for these data was divided into east and west phases of the QBO (defined at 50 hPa), so that power spectra from these two phases could be compared. No obvious differences existed between these two classes of spectra. During El Nino/Southern Oscillation (ENSO) episodes, there was a suggestion of an enhancement of a 20-day signal.

Intraseasonal variability at the equator was investigated using TOMS and MSU-4 data. Power spectra of the two time series with the annual cycle removed are quite "red", with peaks at approximately 15, 20, 40, and 80 days in each time series. A quasi-biennial oscillation (QBO) is evident in both time series, but with much larger amplitude relative to shorter-period fluctuations in the TOMS dataset. Running correlations (180 day) for various bandpass-filtered time series were computed, showing an anticorrelation at 60-90 day periods during the 1983 and 1987 El Nino/Southern Oscillation (ENSO) events, significant at the 1% and 10% levels, respectively. A mechanism for the linkage between the stratospheric data and the ENSO events is being studied.

E. Journal Publications: None.

**A. Title of Research Task:**

The Transient Response to Tropical  
Convective Heating:  
Linear and Nonlinear Aspects

Program No. 579-21-17-70

**B. Investigators and Institutions:**

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**C. Abstract of Research Objectives:**

The objective of the research program is to investigate the nonlinear dynamics associated with the adjustment and equilibration of equatorial stratospheric waves excited by tropospheric convective events. A 3-dimensional primitive equation model of the equatorial lower and middle atmosphere is used to study the response of the tropical stratosphere to prescribed distributions of tropospheric heating. The impact of nonlinearity and transience on the characteristics of the equatorial disturbances is assessed.

#### **D. Summary of Progress and Results:**

1) Simulations have been conducted to assess the impact of self interaction among the spectrum of waves which compose a transient wave packet. The equatorial response to a localized heating distribution in a resting atmosphere has been compared to the response to the Fourier components of the localized heating. Preliminary analysis indicates that nonlinear interaction between wave components leads to changes in the phase speed of the planetary wavenumber 2 component of the transient wave packet.

2) The impact of the LIMS Kalman filtering procedure on Kelvin wave temperature signatures has been explored. The modeled Kelvin wave packet has been inserted into the LIMS temperature retrievals and processed with the Kalman filtering routine used for the archived data sets. Differences between the original Kelvin wave packet and the Kalman filtered Kelvin wave were found to be small between 100 and 10mb. Attenuation of the Kelvin wave signature was largest between 1 and .1 mb. The propagation characteristics of the Kelvin wave packet were not aliased by the LIMS Kalman filter.

3) Simulations have been conducted to investigate the impact of zonal background winds on the evolution of the transient response to equatorial convective heating. Zonal winds and temperatures representative of winter solstice conditions have been imposed as initial conditions for equatorial wave simulations. Significant differences in the characteristics of the transient response were obtained in both the northern and southern hemispheres. Mixed Rossby-gravity wave activity was enhanced in the northern hemisphere westerlies, particularly between 1 and .1 mb. Kelvin wave activity was enhanced in the southern hemisphere easterlies throughout the middle and upper stratosphere. Secondary development was observed in the northern hemisphere westerlies of lower troposphere.

**E. Journal Publications:** None to date



## **Title of Research Task**

Analysis of Stratosphere-Troposphere Exchange

## **Investigators and Institutions**

Leonhard Pfister, NASA/Ames Research Center, Moffett Field, CA  
Henry Selkirk, Space Physics Research Institute, Sunnyvale, CA

## **Abstract of Research Objectives**

The overall goals of this work are to improve our understanding of stratosphere-troposphere exchange, lower stratosphere transport, and the lower stratospheric water budget. We are focusing on: (1) cumulus anvils, believed to be both a major stratospheric dehydration mechanism and a tropical troposphere to stratosphere mass transfer mechanism; (2) convective gravity waves, since their breaking may induce turbulent vertical transport within the lower stratosphere; and (3) the importance of gravity waves and turbulence to cross-jet transport in the high latitude stratosphere. Our primary data sources are the NASA high altitude aircraft field experiments from the Stratosphere-Troposphere Exchange Project (STEP) and the Airborne Arctic Stratosphere Expedition (AASE).

## **Summary of Progress and Results**

Data from the 1987 STEP Tropical field experiment show air masses which are both saturated with respect to ice and significantly drier than values prevailing in the stratosphere. This is the first confirmation of the so-called cold trap mechanism by which tropospheric air is stripped of nearly all its water content. Moreover, the coldest and driest air is found under strongly convective conditions at the very top of cumulus anvils, with tracer mixing ratios and potential temperatures characteristic of surface air. This shows that cumulus anvils can dehydrate tropospheric air to stratospheric humidities. There is evidence for two mechanisms of actual transfer of tropospheric air into the stratosphere associated with convection: (1) radiative heating of the cumulus anvils, causing them to rise into the stratosphere; and (2) direct injection by overshooting convective turrets. Evidence for the first comes from measurements in air masses with stratospheric potential temperatures and tropospheric chemical tracer mixing ratios. Evidence for the second comes from the presence of a 1-2 km thick near-isothermal "transition zone" above convective anvil tops.

The 1987 data also shows the presence of substantial temperature fluctuations due to mesoscale ( 100 km wavelength) gravity waves. Our work has: (1) traced these aircraft-observed gravity waves to convective sources as defined by satellite imagery; and (2) shown that these waves have characteristics consistent with generation by a simple "transient mountain" mechanism. The importance of these mesoscale gravity waves lies in their ability to

deposit momentum at locations far removed from the source region. Our budget study has shown convectively generated mesoscale gravity waves definitely have a significant impact on the momentum budget at 50 km, and may be important to the momentum budget at altitudes as low as 25 km.

Our study of small scale wavelike motions at high latitudes has shown numerous examples of vertically trapped waves. One example is generated by an upward propagating mountain wave. Current theories suggest that vertically propagating gravity waves either propagate conservatively or break down into turbulence; this example suggests a third possibility, namely nonlinear breakdown into trapped waves.

### **Journal Publications**

- Pfister, L., S. Scott, S. Bowen, and M. Legg, 1991: Mesoscale Disturbances in the Tropical Stratosphere Excited by Convection: Observations and Effects on the Stratospheric Momentum Budget. accepted for publication in *J. Atmos. Sci.*
- Russell, P. B., L. Pfister, and H. B. Selkirk, 1991: The tropical experiment of the Stratosphere-Troposphere Exchange Project (STEP): Science Objectives and Operations. submitted to *J. Geophys. Res.*
- Selkirk, H. B., 1991: Temperatures in the lower stratosphere and upper troposphere and the evolution of the Australian monsoon, December 1986 - February 1987. submitted to *J. Geophys. Res.*

A) Title

Large-scale dynamics and transport in the stratosphere

B) Principal Investigator

R. Alan Plumb, Massachusetts Institute of Technology

C) Abstract of Research Objectives

Research conducted during 1990-91 has comprised five investigations of stratospheric dynamics and transport processes: (i) The seasonal cycle of planetary waves in the southern stratosphere and reasons for interhemispheric differences in this cycle; (ii) Large-scale transport in the southern lower stratosphere, especially the redistribution of ozone-poor air during the spring breakdown of the Antarctic polar vortex; (iii) Theory of the mean meridional circulation in the stratosphere; (iv) The impact of tropospheric interannual variability on the stratospheric circulation; and (v) Interrelationships between mixing ratios of long-lived stratospheric tracers.

D) Summary of progress and results

(i) An earlier study of planetary wave behavior in a simple, quasi-linear beta-plane model had found that, with weak tropospheric forcing, a double-peaked (early winter /spring) wave maximum resulted, while a single mid-winter maximum was found when the forcing was strong enough for the wave to limit the strength of the wintertime westerlies. These two cases were superficially similar to southern and northern winter situations, respectively. Studies under this project, however, using a linearized hemispheric model of the southern stratosphere have failed to confirm these beta-plane results. Specifically, while the observed late winter amplification of quasi-stationary planetary waves is reproduced in the model, the early winter amplification is not. The latter conflict is, at present, a mystery.

(ii) In an earlier study of the effects of the December 1987 vortex breakdown in reducing ozone levels in southern midlatitudes, it was found that the horizontal transport of ozone-poor air is necessarily accompanied by midlatitude upwelling. Both have comparable effects in the midlatitude ozone reduction, but only the former is influenced by high-latitude ozone depletion. It is therefore important to be able to understand these separate contributions. Subsequently we have been investigating in more detail the three-dimensional structure of the southern hemisphere final warming. The "omega"-equation has been used in conjunction with potential vorticity calculations based on NMC analyses to identify the vertical motions accompanying the quasi-horizontal redistribution of potential vorticity at such times. At this stage, we have focussed on the vortex breakdown of December 1987 but plan to look at other years in the future. It is also planned to use the three-dimensional picture thus developed to quantify the redistribution of ozone at such times.

(iii) Numerical experiments are being run to investigate the upward effects of zonally-symmetric tropical tropospheric heating on the stratospheric circulation. Model results clearly show that the Hadley cell driven by tropical tropospheric heating does penetrate across the tropopause into the stratosphere and, in fact, may be enough to comprise a significant component of the poleward mass flux in low latitudes. However, the extent and intensity of the penetration shows sufficient sensitivity to such parameters as model viscosity and resolution that we have not yet been able to draw any robust conclusions from this work.

(iv) Much has been done to identify the properties of anomalous, low-frequency, structures in the troposphere. We have extended this procedure into the stratosphere, using NMC stratospheric analyses. We find that these tropospheric anomalies do indeed extend into the stratosphere, as expected for large-scale flow patterns in winter. The amplitudes of these stratospheric anomalies are such that this mode of variability appears to comprise a significant component of the stratospheric total; moreover, a substantial part of the (apparently significant) stratospheric signal *precedes* the appearance of the tropospheric anomaly. This work was completed during the present period.

(v) Analyses of *in situ* measurements of several stratospheric constituents have revealed remarkable, simple relationships between mixing ratios of certain long-lived tracers (*e.g.*,  $\text{N}_2\text{O}/\text{NO}_y$ ,  $\text{N}_2\text{O}/\text{O}_3$ ). In collaboration with Dr Malcolm Ko of AER, Inc., the PI has developed a theoretical interpretation of the remarkable correlations observed between various stratospheric tracers. Thus far, the theory has focussed on a two-dimensional transport formulation, in which it can be shown that a simple dependence between mixing ratios of different long-lived tracers is a direct consequence of the "slope equilibrium" described earlier by others. For very long-lived tracers, the relationship becomes linear. The theoretical predictions have been validated in results from the AER 2D stratospheric chemistry-transport model.

#### E) Journal publications in 1990-91

Turco, R., R.A. Plumb and E. Condon: The Airborne Arctic Stratospheric Expedition: prologue. *Geophys. Res. Lett.*, **17**, 313-316, (1990).

Wirth, V.: What causes the seasonal cycle of stationary waves in the southern stratosphere? *J. Atmos. Sci.*, **48**, 1194-1200 (1991).

Plumb, R.A., and M.K.W. Ko: Interrelationships between mixing ratios of long-lived stratospheric constituents. *J. Geophys. Res.*, (submitted).

## **A . Dynamics of Stratospheric Planetary Waves**

**B . Principal Investigator:** Walter A. Robinson  
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Graduate Research Assistant: Ping Chen  
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**C .** The dynamics of stratospheric planetary waves are studied using a time-dependent, linear, primitive equation model. The time dependence in the model allows the incorporation of realistic wave transience. The goal of the study is to isolate the wave or mean-flow characteristics that determine how much planetary wave activity enters the stratosphere and where in the stratosphere this wave activity is deposited.

**D .** Our linear model (described in Chen 1991) has been used, so far, for three separate studies. In the first of these (Chen and Robinson, 1991a) we considered the influence of wave transience on the propagation of planetary waves. Compared with steady waves, transient wave packets were found to deposit more of their wave activity, and thus their influence on the mean flow, in high latitudes. This high-latitude absorption was found to be associated both with the "non-WKBJ" influence of the local maximum in the Rossby wave refractive index in the jet, and the generation of waves with significant eastward frequencies by the transient forcing.

A second study (Chen and Robinson, 1991b) dealt with the dynamical coupling between the tropical Quasi-biennial Oscillation (QBO) and extra-tropical stratosphere. Two mechanisms for this coupling were found. First, the requirements of potential vorticity conservation and the dynamical balance of the zonal flow lead to small but significant modifications of the extratropical stratosphere, its static stability in particular, by the tropical QBO. Secondly, extra-tropical Rossby waves amplify this signal through their interaction with the modified zonal flow.

For a third study (Chen and Robinson, 1991 c) the lower boundary of the model was moved to the earth's surface, so that the propagation of planetary waves across the tropopause could be studied. The principal finding from this work is the importance of the vertical shear at the high latitude tropopause in determining how much wave activity enters the stratosphere.

Additional work using this model includes the application of the model to observed zonal flows and wave forcing, the generation of eastward propagating waves in the stratosphere, the interference of stationary and transient waves, and comparisons with a new approximate set of equations developed by our colleague, Prof. M. Mak.

**E.**

Chen, P., 1991: *The dynamics of stratospheric planetary waves*. Doctoral dissertation in the Department of Atmospheric Sciences at the University of Illinois. In preparation.

-----, and W. A. Robinson, 1991a: The effects of transience on the propagation of stratospheric planetary waves. *J. Atmos. Sci.*, **48**, 1078-1092.

-----, and -----, 1991b: Dynamical coupling of the extratropical and equatorial quasi-biennial oscillations. *J. Atmos. Sci.*, submitted.

-----, and -----, 1991c: The propagation of planetary waves from the troposphere into the stratosphere. In preparation.

A. Stratospheric General Circulation with Chemistry Model

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- C. The goal of this project is to enhance our understanding of the fully interactive general circulation of the stratosphere. The strategy of investigation is to construct and analyze models of the system and compare with observations. Currently research focuses on realistic transport calculations derived by using meteorological data assimilation techniques.
- D. The recent focus of this effort has been on realistic representation of constituent transport during the 1989 Airborne Arctic Stratosphere Expedition (AASE). The attempt to represent the fundamental processes defined by the high quality in situ data have led to significant reformulation of the model and a major improvement in the ability to simulate stratospheric transport.

The model has been used to investigate the effects of polar heterogeneous chemistry on middle latitudes in the northern hemisphere. The transport of highly processed air to middle latitudes is calculated to occur in selective longitude bands. Initial results suggest that polar processing does not cause the observed middle latitude ozone depletion.

The model has also been used to provide fields to test satellite observation and mapping systems and is a central tool for the assessment of the impact of stratospheric aircraft.

Current research involves longer integrations with full chemistry and detailed studies of stratospheric tropospheric exchange.

## E. Publications

1. "Wintertime Nitric Acid Chemistry: Implications from Three-Dimensional Model Calculations," Richard B. Rood, Jack A. Kaye, Anne R. Douglass, Dale J. Allen, Stephen D. Steenrod, and Edmund M. Larson, *J. Atmos. Sci.*, **47**, 2696-2709, 1990.
2. "Global Three-Dimensional Constituent Fields Derived from Profile Data," A. R. Douglass, R. B. Rood, R. S. Stolarski, M. R. Schoeberl, M. H. Proffit, J. J. Margitan, M. Lowenstein, J. R. Podolske, and S. E. Strahan, *Geophys. Res. Lett.*, **17**, 525-528, 1990.
3. "Three Dimensional Simulation of Hydrogen Chloride and Hydrogen Fluoride During the Airborne Arctic Stratosphere Expedition," Jack A. Kaye, Anne R. Douglass, Richard B. Rood, Richard S. Stolarski, Paul A. Newman, Dale J. Allen, Edmund M. Larson, Michael T. Coffey, William G. Mankin, and Geoffrey C. Toon, *Geophys. Res. Lett.*, **17**, 529-532, 1990.
4. "The Influence of Polar Heterogenous Processes on Reactive Chlorine at Middle Latitudes: Three-dimensional Model Implications", Anne R. Douglass, Richard B. Rood, Jack A. Kaye, Richard S. Stolarski, Dale J. Allen, and Edmund M. Larson, *Geophys. Res. Lett.*, **18**, 25-28, 1991.
5. "Spatial and Temporal Variability of the Extent of Chemically Processed Stratospheric Air," Kaye, J. A., A. R. Douglass, R. B. Rood, R. S. Stolarski, P. A. Newman, D. J. Allen, and E. M. Larson, *Geophys. Res. Lett.*, **18**, 29-32, 1991.
6. "Three Dimensional Simulation of Wintertime Ozone Variability in the Lower Stratosphere," Richard B. Rood, Anne R. Douglass, Jack A. Kaye, Marvin A. Geller, Chi Yuechen, Dale J. Allen, Edmund M. Larson, Eric R. Nash and J. Eric Nielsen, *J. Geophys. Res.*, **96**, 5055-5072, 1991.
7. "Application of a Monotonic Upstream Transport Scheme to Three Dimensional Constituent Transport Calculations," Dale J. Allen, Anne R. Douglass, Richard B. Rood, and Paul D. Guthrie, *Mon. Wea. Rev.* (to appear), 1991.
8. "Three-dimensional Constituent Transport Models and the Study of Interannual Variability," Richard B. Rood, *J. of Geomagnetism and Geoelectricity* (to appear), 1991.
9. "Episodic Total Ozone Minima and Associated Effects on Heterogeneous Chemistry and Lower Stratospheric Transport," Richard B. Rood, J. Eric Nielsen, Richard S. Stolarski, Anne R. Douglass, Jack A. Kaye, and Dale J. Allen, *J. Geophys. Res.* (to appear), 1990.



**A. Stratospheric Data Analysis System (STRATAN)**

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- C.** The goal of this project is to produce state-of-the-art stratospheric analyses using a coupled stratosphere troposphere data assimilation system (STRATAN). This effort focuses on the use of assimilated data in other than its traditional venue of numerical weather prediction. A particular emphasis are the global transport characteristics of the atmosphere as revealed by constituent measurements.
- D.** Two long assimilation experiments (December 1978 - May 1979 and January 1989 - March 1989) have been completed. These are currently being used in stratospheric and tropospheric transport calculations. The data sets have been distributed to 10 investigators nationwide.

A series of experiments to assess the impact of the proposed EOS instrument SWIRLS has been completed. These results were discussed in a workshop held at Goddard in December 1990 chaired by R. Lindzen and D. McCleese.

Recently the system has been updated and moved to the new Cray. After further testing the new system will be used to reprocess the old data as well as to provide a multiyear data set.

E. Publications

1. "Stratospheric Temperatures During AASE: Results from STRATAN," Richard B. Rood, Paul A. Newman, Leslie R. Lait, David J. Lamich, and Roland Chan, *Geophys. Res. Lett.*, **17**, 337-340, 1990.
2. "Three Dimensional Simulation of Wintertime Ozone Variability in the Lower Stratosphere," Richard B. Rood, Anne R. Douglass, Jack A. Kaye, Marvin A. Geller, Chi Yuechen, Dale J. Allen, Edmund M. Larson, Eric R. Nash and J. Eric Nielsen, *J. Geophys. Res.*, **96**, 5055-5072, 1991.
3. "Three-dimensional Constituent Transport Models and the Study of Interannual Variability," Richard B. Rood, *J. of Geomagnetism and Geoelectricity* (to appear), 1991.
4. "The Minor Stratospheric Warming of January 1989: Results from STRATAN, a Stratospheric/Tropospheric Data Assimilation System," Stephen D. Steenrod, Richard B. Rood, David J. Lamich, Joan E. Rosenfield, and Ravi C. Govindaraju, *Mon. Wea. Rev.* (to appear), 1991.

## BIENNIAL RESEARCH SUMMARY

### **A. Grant Title:** Irreversible Transport Associated with Planetary Waves

Number: NAGW-772

CU Number: 1533103

### **B. Investigators:**

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**C. Research Objectives:** The research program focuses on horizontal air motions associated with planetary waves and their interaction with radiation and chemistry in the stratosphere.

**D. Progress:** Research published during 1990 – 1991 reflects investigation of eddy air motions along several avenues. A series of numerical calculations using an equivalent-barotropic model explore the role of horizontal mixing by planetary waves and how it is influenced by diabatic effects in the stratosphere. According to the numerical calculations, dispersive air motions prevail only at low latitudes, where temperature perturbations associated with eddy disturbances are small and thermal dissipation is inefficient. This simplified numerical framework reproduces essential features of the time-mean circulation in the stratosphere. The impact of large-scale transience on these processes was explored in calculations where planetary wave unsteadiness was represented in terms of a monochromatic traveling (e.g., like the 16-day wave) and in terms of stochastic variability typical of random fluctuations in the stratosphere. Calculations with the equatorial flow restored to conditions typical of either the easterly or westerly phase of the quasi-biennial oscillation (QBO) were used to demonstrate that planetary wave transport can account for the observed QBO in the extratropical circulation.

One of the virtues of the equivalent-barotropic framework is that it accounts for compressibility as air moves vertically, e.g., along isentropic surfaces. This feature of the system was used to simulate large fluctuations in total ozone that are observed at high latitudes during sudden stratospheric warmings. Similar behavior has been diagnosed in recent work with TOMS data.

Kelvin waves observed in LIMS data lead to temperature fluctuations in the tropical stratosphere in excess of 5 K. A study based on constituents observed by LIMS reveal that Kelvin

wave temperature fluctuations and the corresponding fluctuations in transport produce a clear signal in the distribution of ozone as well as in other species.

Recent work on correlations between solar activity and various barometers of atmospheric behavior have revived interest in solar-terrestrial relationships. Until recently, these correlations have defied explanation. A statistical analysis demonstrated that the dramatic increase in correlation with solar activity that results when data are stratified according to the phase of the QBO results as an artifact of periods near the solar cycle being aliased by the QBO.

The traditional scheme for inferring air motion from space relies upon measurements of temperature and simple forms of momentum balance like geostrophy which must be prescribed but which are not uniformly valid. Predicated on measurements of tracer behavior, made ideally aboard multiple orbiting platforms, a new algorithm for retrieving the motion field from space has been developed. Since it is based on direct observations of the material behavior and does not rely on artificially-prescribed relationships to infer motions, this approach circumvents many of the limitations inherent of the traditional scheme.

#### E. Publications:

- O'Sullivan, D. and M. Salby, 1990: Coupling of the quasi-biennial oscillation and the extratropical circulation in the stratosphere through planetary wave transport. *J. Atmos. Sci.*, **47**, 650–673.
- \_\_\_\_\_, R. Garcia, D. O'Sullivan, and J. Tribbia, 1990: Global transport calculations with an equivalent barotropic system. *J. Atmos. Sci.* **47**, 188–214.
- \_\_\_\_\_, D. O'Sullivan, R. Garcia, and P. Callaghan, 1990: Air motions accompanying the development of a planetary wave critical layer. *J. Atmos. Sci.*, **47**, 1179–1204.
- \_\_\_\_\_, D. O'Sullivan, R. Garcia, and P. Callaghan, 1990: The interaction of horizontal eddy transport and thermal drive in the stratosphere. *J. Atmos. Sci.*, **47**, 1647–1665.
- \_\_\_\_\_, and R. Garcia, 1990: Dynamical perturbations to the ozone layer. *Physics Today*, **43**, 38–46 (cover).
- \_\_\_\_\_, P. Callaghan, and S. Solomon, and R. Garcia, 1990: Chemical fluctuations associated with vertically propagating equatorial Kelvin waves. *J. Geophys. Res.*, **95**, 20491 – 20505.
- \_\_\_\_\_, and R. Garcia, 1990: Dynamical perturbations to the ozone layer. *Parity*, **43**, 2–12 (Japanese).
- \_\_\_\_\_, 1991: The influence of planetary wave transience on horizontal air motions in the stratosphere. *J. Atmos. Sci.* (in press).
- \_\_\_\_\_, and D. Shea, 1991: Correlations between solar activity and the atmosphere: An unphysical explanation. *J. Geophys. Res.* (in press).
- Callaghan, P. and \_\_\_\_\_, 1991: Fluctuations in total ozone and their relationship to stratospheric air motions. *Science* (to be submitted).
- Juckes, M. and \_\_\_\_\_, 1991: An algorithm for deriving the motion field from satellite measurements of tracer behavior. *J. Geophys. Res.* (to be submitted).

## STRATOSPHERE-TROPOSPHERE EXCHANGE DURING HIGH-LATITUDE CYCLOGENESIS

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**Abstract** Recently, we have observed that stratospheric air can descend into the marine boundary layer during intense mid-latitude cyclogenesis. More recently, both model studies and in situ aircraft measurements have provided data which suggests that stratospheric values of potential vorticity are being generated at low levels (900 mb) in rapidly deepening oceanic cyclones. This may provide a mechanism for direct and immediate transport of mid-latitude lower tropospheric air into the stratosphere.

Results from a NOAA WP-3D aircraft (Fig. 1) show an intrusion of stratospheric ozone extending to the sea surface within a frontal zone and associated tropopause fold over the eastern Pacific Ocean. This is the first evidence of stratosphere to sea surface transport of ozone of this nature.

Our numerical simulations with the Penn State/NCAR mesoscale prediction model show the role of latent heating within extratropical marine cyclones in producing secondary tropopause folds and associated stratospheric-tropospheric exchange during extreme cyclogenetic events. Comparisons with TOMS ozone analyses confirm this process as evidenced by the development of large, narrow, ozone gradients in the region of secondary tropopause folding.

While studying stratospheric-tropospheric exchange in the south polar regions, it was discovered that austral summer tropospheric ozone has been decreasing steadily at South Pole over the past decade in concert with the timing and extent of the stratospheric ozone hole due to increased UV. As shown in Fig. 2, the observed 17% decrease in austral summer ozone concentrations is closely associated with a 25% increase in observed cloudiness over the same period.

### ***Publications***

Bond, N.A., and M.A. Shapiro, Research aircraft observations of the mesoscale and microscale structure of a cold front over the Eastern Pacific Ocean. In press, Mon. Wea. Rev., Dec. 1991.

Li, S.-M., J.W. Winchester, J.D. Kahl, S.J. Oltmans, R.C. Schnell, and P.J. Sheridan, Arctic boundary layer ozone variations associated with nitrate, bromine, and meteorology: A case study. J. Geophys. Res., **95**, 22,433-22,440, 1990.

Schnell, R.C., S.C. Liu, S.J. Oltmans, R.S. Stone, D.J. Hofmann, E.G. Dutton, T. Deshler, W.T. Sturges, J.W. Harder, S.D. Sewell, M. Trainer, and J.M. Harris, Decrease of summer tropospheric ozone concentrations in Antarctica. Nature, **351**, 726-729, 1991.

Shapiro, M.A., E. Donall, P.J. Neiman, and R. Bleck, A numerical simulation of extratropical marine cyclogenesis: A potential vorticity perspective. Manuscript, Mon. Wea. Rev., 1991.

# **Studies of Large Scale Stratospheric Dynamics Using a Numerical Model Coupled with Observations**

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**Research Objectives:** The research addresses questions of the interaction of planetary waves with the mean flow in the stratosphere. Experiments are run with a numerical model extending through the middle atmosphere. Observed zonal mean fields are used in the model to investigate the dependence of wave propagation and wave - mean flow interaction on the basic state for observed cases. The primary focus of the study is to investigate 1) the role of preconditioning and/or resonance in observed sudden stratospheric warmings; 2) the effect of stratospheric flow structure on planetary wave propagation in the troposphere; and 3) the impact of tropical and subtropical wind variations on waves in the winter hemisphere.

**Progress and Results:** The original plan called for using a quasi-geostrophic wave model along with observations in order to investigate some questions of wave-mean flow interaction in the extratropical winter stratosphere. The dynamical events during sudden warmings can be strongly influenced by the presence of critical lines (where the wave phase speed is equal to the zonal wind speed) in the very region where the wave-mean flow interaction was occurring. The treatment of critical line behavior in a simple wave model is approximate at best, and may in fact give inaccurate results. Because of the possibility that the model treatment of critical line interactions exerted a controlling influence on the atmospheric dynamics, a more accurate model was needed for wave-mean flow interaction studies. A new model was adapted from the 3-dimensional primitive equation model developed by K. Rose and G. Brasseur.

The 3-d model is hemispheric and extends from 10 to 80 km. The temperature, geopotential and three components of the wind are computed from the primitive equations, written in flux form. The resolution of the model is  $11.25^\circ$ ,  $5^\circ$  and about 3 km in the zonal, meridional and vertical directions, respectively. The model is "mechanistic" in the sense that the dynamical evolution is determined in large part by the evolution of the lower boundary, which is specified. In the present application, the model is used to simulate specific sequences of dynamical events. For this, the model is initialized with dynamical/thermodynamic fields deduced from the temperature and geopotential measurements for a particular day. The lower boundary is taken from the evolution of the 250 mb geopotential beginning on the initialization day. In addition to the boundary forcing,

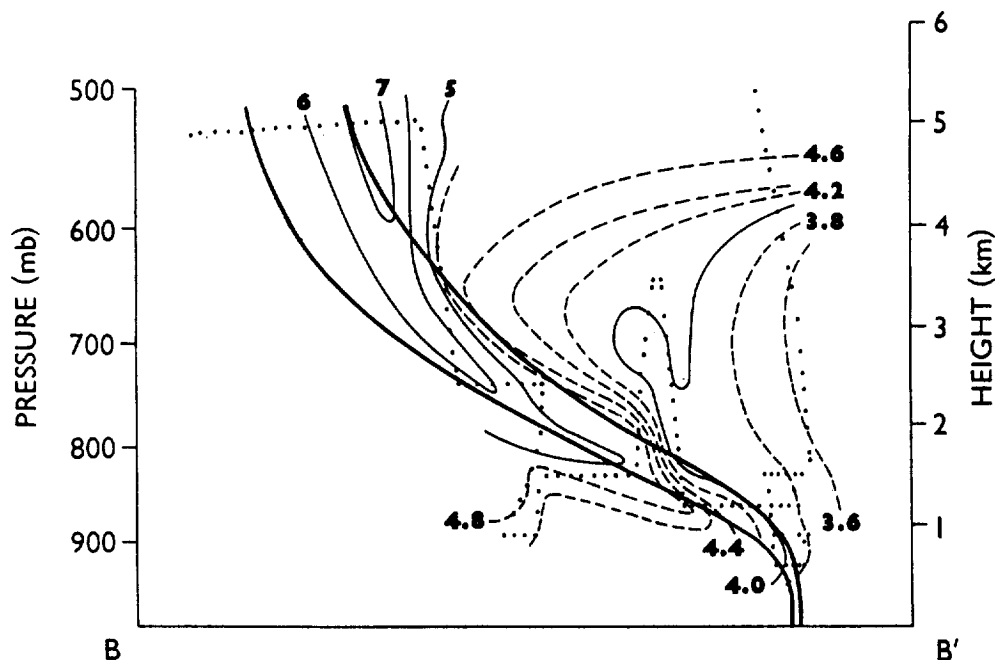


Fig. 1. Cross-section analysis of ozone ( $\text{pphm vol}^{-1}$ ) in relation to a cold frontal boundary (heavy lines) in the Eastern Pacific measured with a NOAA WP-3D. Solid ozone isolines refer to whole units of  $\text{pphm vol}^{-1}$ , dashed lines are intermediate contours. Note the tongue of ozone projecting to the sea.

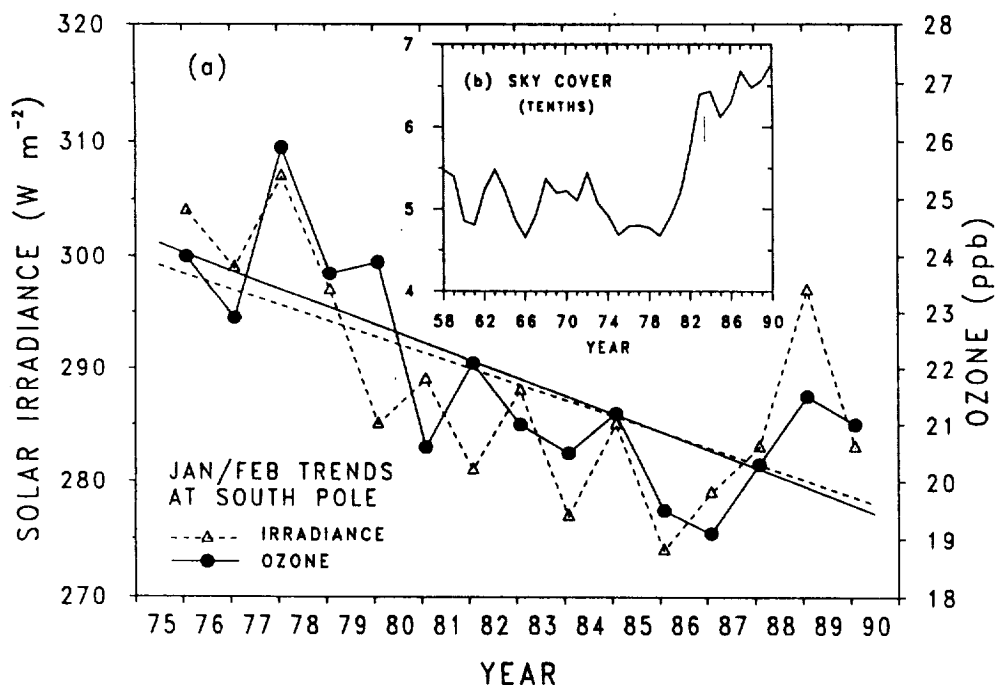


Fig. 2. Mean surface ozone concentrations and linear trend in January and February (dots and solid line, referenced to right scale) compared with the mean January-February solar irradiance flux and linear trend (triangles and dashed lines, referenced to left scale), measured at the South Pole from 1976 to 1990. The data points are plotted for 31 January of each year. Inset, long-term (1958-90) record of January-February sky cover at the South Pole.

the model evolution is controlled by the diabatic forcing. The present version represents the diabatic effects by a Newtonian cooling relaxation to a climatological (zonal mean) temperature. A new version is being developed that determines  $O_3$  and  $O_2$  heating from climatological values and uses the precomputed transmission functions from the GFDL GCM to calculate  $CO_2$  cooling.

A look at the NMC data for the period 1978-1989 indicates many similarities between the warmings of February, 1979 and February, 1989. Both began when the zonal mean wind profile was characterized by a high latitude jet in the lower stratosphere ( $\sim 10$  mb,  $65-70^\circ N$ ) with near-zero or negative (easterly) winds extending quite far into the winter hemisphere from the tropics, and with very weak wind speeds near the stratopause. In both warmings, wave 2 was dominant, although the 1989 warming it did not have the eastward phase progression seen in 1979. Simulations with the 3-d model (without chemistry), initialized with NMC data from a week before each of these two warmings, indicate that the stratospheric flow had been preconditioned for a warming. Additional numerical integrations indicated that the preconditioning did not depend on the details of the wave pulse that caused the warming and that it was more sensitive to the flow in the lower stratosphere than to that in the upper stratosphere.

### ***Publications***

Smith, A. K., Preconditioning for sudden stratospheric warmings: Sensitivity studies with a numerical model. submitted to *J. Atmos. Sci.*, April, 1991.



A Proposal to Investigate the Generation, Propagation, and Effects of Internal Gravity Waves in the Stratosphere Using Numerical Models and Observational Data

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Co-Investigator: Dr. Julio T. Bacmeister  
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RESEARCH OBJECTIVES: A high resolution, time dependent, nonlinear, 2-dimensional gravity wave model and a linear, steady-state, 3-dimensional mountain wave model will be used in a coordinated series of investigations to understand the role of gravity wave forcing, propagation, breakdown and transport in the stratosphere. These investigations will utilize observational data from STEP, AASE, and AAOE aircraft experiments to verify model results and to develop parameterization schemes for gravity wave stress and transport for use in general circulation models. Among the primary objectives of this project will be to estimate the amount of gravity wave momentum flux escaping from the troposphere as a function of mean flow conditions and topography. Results from this investigation will also help to clarify the effect of small-scale (<100 km) variability on the transport and microphysics of aerosols and PSC's in the stratosphere.

SUMMARY OF PROGRESS AND RESULTS: Analysis of data collected in the Antarctic and Arctic lower stratosphere during NASA's AAOE and AASE aircraft campaigns was performed to understand what part small-scale wave motions generated by mountains contribute to weather in the polar stratosphere when ozone depletion occurs. The data studied consisted primarily of temperature cross-sections taken by a microwave temperature profiler on board an ER-2 high-altitude airplane. These cross sections gave a good picture of wave activity within 3 km above and below the airplane. Wave activity was found to have a significant relationship to topography and the local winds between the surface and 20 km. Computer models of mountain waves were used to simulate wave activity and interpret the data. Calculations suggested that low-level blocking may be an important mechanism in controlling the amplitude of mountain waves in the Antarctic.

A detailed analysis of mountain wave propagation through observed, global wind and temperature fields was performed to determine mountain wave drag on winds in the stratosphere and mesosphere. Most drag in the southern hemisphere originates over the southern Andes and Antarctic Peninsula, whereas in the northern hemisphere planetary waves modulate the magnitude and distribution of mountain wave drag.

JOURNAL PUBLICATIONS

Bacmeister, J. T., M. R. Schoeberl, L. R. Lait, P. A. Newman, and B. Gary, ER-2 mountain wave encounter over Antarctica: Evidence for blocking, Geophys. Res. Lett., 17, 81-84, 1990.

Bacmeister, J. T., M. R. Schoeberl, L. R. Lait, P. A. Newman, and B. Gary, Small-scale waves encountered during AASE, Geophys. Res. Lett., 17, 349-352, 1990.

Bacmeister, J. T., Mountain-wave drag in the stratosphere and mesosphere inferred from observed winds and a simple mountain wave parameterization scheme, J. Atmos. Sci., in press, 1991.



B. STRATOSPHERIC CHEMISTRY, ANALYSIS  
AND RELATED MODELING

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#### A. Satellite Study of Mesospheric Ozone

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#### C. RESEARCH OBJECTIVES

The ultraviolet spectrometer polarimeter, UVSP, instrument on the SMM spacecraft has been used in a solar occultation mode to obtain mesospheric ozone measurements in the 50 to 70 km altitude region. Data were obtained from 1985 through 1989 providing an opportunity to observe the mesosphere from a period of low solar activity until high solar activity in 1989. Mesospheric ozone properties studied included: sunrise-sunset differences, the presence of wave activity as a function of latitude and longitude, and long-term behavior including response to solar activity. Data were coordinated with mesospheric temperatures from other satellite and ground-based sources. Photochemical model simulations mesospheric ozone behavior will be compared with data in order to validate ozone production and loss processes.

#### D. SUMMARY OF PROGRESS AND RESULTS

The behavior of mesospheric ozone from 1985 through 1989 have been analyzed using data from the UVSP/SMM solar occultation experiment. The seasonal behavior of low-latitude,  $\pm 30^\circ$ , 50 to 70 km altitude reveals several interesting features. Annual as well as semiannual waves are observed in the 50 to 70 km altitude region. In the latitude range of  $\pm 30^\circ$  the ozone phase and amplitude are functions of temperature and seasonal changes in solar flux. Temperature is the controlling factor for the equatorial region and seasonal changes in solar flux become more dominant at latitudes outside the equatorial zone (greater than  $\pm 15^\circ$ ). There is a hemispheric asymmetry in the ozone annual wave in the  $20^\circ$  to  $30^\circ$  region, with northern hemispheric ozone having a larger amplitude than southern hemispheric ozone. In this region temperature is nearly in phase with ozone in both hemispheres and is reduced in amplitude in the northern hemisphere. The equatorial region is characterized by a strong semiannual wave in addition to the annual variation, and temperature is nearly out of phase with ozone.

At all latitudes there is a larger ozone concentration at sunrise than at sunset. The sunrise-sunset difference increases with increasing altitude. At 55 km differences are only 10%, but at 60 km there is 25% more ozone at sunrise than at sunset. The difference at 65 km is 40%.

The beginning of the data acquisition period in 1985 corresponded to a period of low solar activity and the minimum in the sunspot cycle was reached in 1986. Solar activity increased after that and was near maximum in late 1989 when data gathering ended with spacecraft reentry into the atmosphere. Between the latitudes of  $\pm 20^\circ$  ozone exhibits an upward trend from 1985 through 1989. The trend is larger at higher altitudes and also increases from southern latitudes across the equator into northern latitudes. It is always positive varying from 0.6% per year at  $20^\circ\text{S}$  and 55 km to 1.1% per year at  $20^\circ\text{N}$ . At the equator and 55 km the trend is 0.9% per year while at 62 km at the same location the trend is 1.9% per year.

In order to understand ozone changes a study was performed of long term temperature changes in the lower mesosphere. The largest atmospheric temperature changes due to the increase of greenhouse gases are expected in the 40 to 60 altitude region, where enhanced infrared cooling decreases the temperature. Ten-year (1980-1990) temperature trends at 55 km and 0.4 mb, derived using data from the ground-based lidar at Haute Provence,  $44^\circ\text{N } 6^\circ\text{E}$ , and the SSU channel 47X

on several satellites, are presented. These data show temperature decreases that are as large and in some cases exceed predictions based on current models. At 44°N, the ground-based lidar and satellite techniques give a negative trend of  $-0.10 \pm 0.04\%$  per year and  $-0.14 \pm 0.02\%$  per year, respectively. Agreement between these two data sets is based on difference measurement techniques gives confidence in the detected trends at this latitude. Further analysis of the SSU 47X satellite data between 45°S and 45°N indicates a maximum decline of 0.16% per year near 30°N. A minimum trend decrease of 0.07% per year is detected between 20° and 30°S. Based on NOAA satellite radiance observations, these long-term temperature changes are larger than changes at any of the other stratospheric levels below 55 km monitored during this period.

These temperature changes are consistent with the observed ozone increases over the 1985-1989 period. However, because solar flux increases between 1986 and 1989 will lead to mesospheric ozone increases no estimate has been made of the contribution by the secular temperature decrease.

#### E. PUBLICATIONS

1. Aikin, A. C., W. Henze, D. Kendig, R. Nakatsuka, and H. J. P. Smith, "Variations of Mesospheric Equatorial Ozone Observed by the Solar Maximum Mission," *Geophys. Res. Lett.*, **17**, 299-302, 1990.
2. Aikin, A. C., M. L. Chanin, J. Nash, and D. J. Kendig, "Temperature Trends in the Lower Mesosphere," *Geophys. Res. Lett.*, **18**, 235, 1991.
3. Aikin, A. C., and D. J. Kendig, "Low-Latitude Behavior of Mesospheric Ozone as Observed by SMM," *J. Atmos. Terr. Phys.* (accepted), 1991.

Grant NAGW-2563

Nitric Oxide Fluxes into the Middle Atmosphere

Investigator:

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Abstract:

In this project, the global thermospheric nitric oxide is investigated using satellite nitric oxide data sets and theoretical models of the chemistry and dynamics of the upper atmosphere. Nitric oxide (NO) plays an important role in the chemistry and thermal structure of the upper atmosphere. NO is efficiently produced in the thermosphere, particularly at auroral latitudes, and may be transported downward to stratospheric altitudes, where it may increase the destruction of ozone. The magnitude of this effect is in question, however, because the NO flux into the lower atmosphere is not known. Determination of the NO fluxes also impact theoretical modelling of the stratosphere and mesosphere since these models require the thermospheric NO flux as part of the model boundary conditions. In this project, the global nitric oxide flux from the thermosphere into the mesosphere is investigated using satellite nitric oxide data sets and theoretical models of the chemistry and dynamics of the upper atmosphere. The study will allow a determination of the NO fluxes as a function of latitude, season, and solar cycle. Geomagnetic activity effects may also be discerned.

Summary of Progress and Results:

Thus far the NO distribution has been computed with a two-dimensional model for solstices for solar cycle minimum and maximum conditions. The fluxes from the upper to the lower atmosphere are therefore also available for these two periods.

A state-of-the-art three-dimensional model, the National Center for Atmospheric Research Thermosphere/Ionosphere General Circulation Model, has been modified to calculate odd nitrogen densities. Model runs have been obtained for a variety of conditions, including equinox and solstice for solar cycle minimum and maximum for geomagnetically quiet, moderate, and disturbed conditions. Testing and validation of the model runs has awaited arrival of the grant funds, which only occurred in July 1991.

Publications:

None yet, since the funds for this project only became available July 1991.

## A. ER-2 Polar Ozone Studies

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## C. Research Objectives

The NASA Airborne Arctic Stratospheric Expedition(AASE) was completed in early 1989. The mission utilized the NASA ER-2 aircraft to gather constituent data in the high latitude stratosphere during winter in an effort to learn more about the ozone depletion in this region. The effort since then has been to use the data to evaluate the chemical and dynamical environment of the Arctic stratosphere, its potential for ozone destruction, and the processes that underlie this destruction. Techniques used in the approach are to formulate and interpret relationships between measured constituents, make comparisons of data with photochemical and meteorological models, and contrast the data and results with that gathered earlier in the southern hemisphere winter region.

## D. Summary of Progress and Results

Chemical perturbations were found in the 1989 Arctic vortex that provide potential for ozone destruction. Evidence of ozone loss in the Arctic vortex can be deduced from changes in the correlation of ozone with nitrous oxide, a conserved tracer. From 410 to 490 K potential temperatures outside the vortex, ozone and nitrous oxide exhibit a linear relationship for all values. Inside the vortex, ozone values are reduced up to 35% compared to values outside at similar nitrous oxide values. Using this relation, a comparison of in situ ozone values with lidar soundings of ozone show comparable loss features of about 17% in January near 20 km altitude. In another approach, differences in the temporal trends of nitrous oxide and ozone on potential temperature isentropes indicate descent of air parcels in the winter season as well as a net loss of ozone of about 0.4% per day in early 1989. Modeling of the photochemistry along isentropic trajectories that intersect the ER-2 flight track was also performed. ER-2 constituent data was used to constrain the final conditions in air parcels during a simulation of several model days. Results indicate that the abundances of reactive nitrogen and chlorine lead to ozone loss of near 1% per day, consistent with the other assessments.

Chemical perturbations in the Arctic include the removal of reactive nitrogen and the repartitioning of the reactive nitrogen reservoir. Removal occurs from the condensation of nitric acid, a major component of the reservoir, on pre-existing sulfate aerosols and the sedimentation of these particles to lower levels. Removal of reactive nitrogen was quantified by its relationship with nitrous oxide in a similar manner to the ozone/nitrous oxide relation. These relationships are common to both hemispheres and are supported by photochemical model simulations of the stratosphere. Removal of up to 90% of the nitrogen reservoir was observed at times, but such observations were relatively less frequent than in the Antarctic region. Removal of water vapor by sedimentation was slight, in sharp contrast to the large removal observed in the Antarctic. Removal of reactive nitrogen without significant water removal suggests that selective nucleation of background sulfate aerosols must occur to limit particle growth to a small fraction of available sites. The differences observed between hemispheres are attributed to Arctic winters that are shorter and that generally have higher temperatures that limit condensation. In addition to removal of reactive nitrogen, the latitude dependence of the ratio  $\text{NO}_x/\text{NO}_y$  decreased poleward, indicating the repartitioning of the reservoir to favor higher oxides such as  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$ .

The distribution of water vapor is highly asymmetric between the hemispheres. In the Antarctic, evidence of dehydration is observed both inside and outside the polar vortex. This implies that air is dehydrated at low temperatures inside the vortex and transported outside where temperatures are



higher. In the Arctic vortex, little evidence of dehydration is observed while values of residual water indicate a non-tropical entry point for some of the air in the stratosphere. However, a dehydration mechanism was inferred from occasional observations of large aerosol particles that were correlated with ice saturation at higher levels. This suggests that ice particles are formed at these levels and sediment in the sampled air parcels. The asymmetry in water vapor is maintained in the troposphere where values in the Arctic are from 2 - 4 times greater than values in the Antarctic. The higher values at the Arctic tropopause lead to more frequent occurrences of ice saturation. These observations set important boundary conditions for climate models simulating the role of water vapor as a greenhouse gas.

#### E. Selected Publications

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- Dye, J.E. et al., Observed particle evolution in the polar stratospheric cloud of January 24, 1989, *Geophys. Res. Lett.* **17**, 413-416(1990).
- Fahey, D.W. et al., Nitric oxide measurements in the Arctic winter stratosphere, *Geophys. Res. Lett.* **17**, 489-492(1990a).
- Fahey, D.W. et al., Observations of denitrification and dehydration in the winter polar stratospheres, *Nature* **344**, 321-324(1990b).
- Fahey, D.W. et al., A diagnostic for denitrification in the winter polar stratospheres, *Nature* **345**, 698-702(1990c).
- Gandrud, B.W. et al., The January 30, 1989 Arctic Polar Stratospheric Clouds(PSC) event: Evidence for a mechanism of dehydration, *Geophys. Res. Lett.* **17**, 457-460(1990).
- Jones, R.L. et al., The polar stratospheric cloud event of January 24, Part 2, Photochemistry, *Geophys. Res. Lett.* **17**, 541-544(1990).
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- Kelly, K.K. et al., A comparison of ER-2 measurements of stratospheric water vapor between 1987 Antarctic and 1989 Arctic Airborne Missions, *Geophys. Res. Lett.* **17**, 465-468(1990a).
- Kelly, K.K. et al., Wintertime asymmetry of upper tropospheric water between the Northern and Southern hemispheres, *Nature* **353**, 244-247(1991).
- McKenna, D.S. et al., Calculations of ozone destruction during the 1988/89 Arctic winter, *Geophys. Res. Lett.* **17**, 553-556(1990).
- Murphy, D.M., Ice saturation at the tropopause observed from the ER-2 aircraft, *Geophys. Res. Lett.* **17**, 353-356(1990).
- Proffitt, M.H. et al., Ozone loss in the Arctic polar vortex inferred from high-altitude aircraft measurements, *Nature* **347**, 31-36(1990).
- Schoeberl, M.R. et al., Stratospheric constituent trends from ER-2 profile data, *Geophys. Res. Lett.* **17**, 469-472(1990).

A. Modeling of the partitioning of reactive nitrogen in the lower stratosphere.

B. D.W. Fahey and S.R. Kawa

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C. Research Objectives

Partitioning of the major components of the reactive nitrogen and inorganic chlorine reservoirs is derived from measurements in the lower stratosphere. The measurements are made from the NASA ER-2 aircraft platform during the winter season in both hemispheres at latitudes of about 60 to 80 degrees. The approach uses the correlated set of measurements to extend what can be learned from looking at measurements of individual species. The results provide a consistent method for comparing distributions, and hence the controlling processes, between different areas of the near polar regions.

D. Summary of Progress and Results

The partitioning of the  $\text{NO}_y$  and  $\text{Cl}_y$  reservoirs has been derived in a consistent manner for winter high latitudes in both hemispheres. Values for  $\text{NO}_2$ ,  $\text{ClONO}_2$ ,  $\text{N}_2\text{O}_5$ , and  $\text{Cl}_2\text{O}_2$  were derived from the measured quantities  $\text{NO}$ ,  $\text{O}_3$ , pressure and temperature using known reaction rates and modeled photodissociation rates. The approach follows that of an earlier study using midlatitude data [Kawa et al., 1990]. Values for the reservoir totals are independently obtained from the aircraft measurements of  $\text{N}_2\text{O}$ , organic chlorine, and  $\text{NO}_y$ . The relative fractions of the measured and derived species within their respective reservoirs are calculated and the longer lived species,  $\text{HNO}_3$  and  $\text{HCl}$ , are estimated as the residuals of the reservoir totals.

The resulting latitude distributions in the Arctic outside the vortex agree well with predictions of a 2D photochemical model, indicating that partitioning in this region is largely controlled by standard homogeneous gas phase chemistry. Inside the Arctic vortex, a large fraction of the  $\text{HCl}$  has been converted to reactive chlorine species  $\text{ClO}$  and  $\text{Cl}_2\text{O}_2$ , consistent with the extensive action of known heterogeneous reactions, presumably occurring on the surfaces of polar stratospheric clouds formed in the cold temperatures of the vortex. Partitioning in the Antarctic suggests that nearly the entire range of latitudes sampled by the ER-2 is affected by heterogeneous processes.

E. Publications

Kawa, S.R. et al., Interpretation of aircraft measurements of  $\text{NO}$ ,  $\text{ClO}$ , and  $\text{O}_3$  in the lower stratosphere, *J. Geophys. Res.* **95**, 18597-18609(1990).

Kawa, S.R. et al., Photochemical partitioning of the reactive nitrogen and chlorine reservoirs in the high latitude stratosphere, *J. Geophys. Res.*, in press(1991).

**A. Further Studies of Tropospheric Chemistry Using Satellite Data Sets**

**B. Jack Fishman, Principal Investigator**  
NASA Langley Research Center

**C. Abstract of Research Objectives:**

Because the primary intent of the measurement of total ozone was for the study of the distribution of stratospheric ozone, little research was conducted using the information provided by TOMS in the Tropics. In research we initiated in 1984, it was noted that the variability in the total ozone distribution at low latitudes was likely a manifestation of the variability of tropospheric ozone. The use of TOMS for tropospheric studies was taken a step further when data from the Stratospheric Aerosol and Gas Experiment (SAGE) were used to derive the amount of ozone in the stratosphere. Ozone measurements from the SAGE instruments (SAGE was launched in February 1979 and operated through November 1981; SAGE II was launched in November 1984 and is still operating) provide the vertical distribution of ozone in the stratosphere. From these profiles, the amount of ozone in the stratosphere (i.e., from the tropopause to ~55 km) could be integrated and then subtracted from the co-located total ozone amount derived independently from the TOMS on the same day. Although these two quantities are nearly equal, and the subsequent subtraction of two relatively large numbers does not appear to be capable of yielding very accurate results (both instruments claim a precision of 3 percent), the resultant distribution of the tropospheric residual displayed remarkable patterns when examined as a function of latitude and longitude. The primary findings of this analysis include the identification of distinct plumes that seem to result from pollution originating over North America, Asia, Africa, and Europe. In the three northern continents, contours of more than 40 D.U. (Dobson Units) originate over the eastern portions of each land mass during both spring (March-May) and summer (June-August) and are transported by the prevailing westerlies for several thousand km. The amount of tropospheric ozone is most pronounced in summer where some amounts above 50 D.U. are seen over Europe and downwind of Asia. At low latitudes, the highest concentrations of the tropospheric residual are off the west coast of Africa. This research will utilize the tropospheric residual data described above to provide even better insight into global and regional scale tropospheric chemistry.

**D. Summary of Progress and Results**

Since funding was received in March 1991, the tropospheric residual data set has been recalculated using the Version 6.0 release of the TOMS archive. Analysis of this new data set, which goes through May 1990 is continuing. Using the Version 6.0

data, we have initiated trend analysis of the tropospheric residual. Also, we have done a preliminary analysis of SAGE II ozone profiles for the upper troposphere in the Tropics. The initial results from these data indicate a substantial qualitative difference between the amount of ozone in the upper troposphere over the tropical Atlantic Ocean in September-October and the amount of ozone in the upper troposphere over the equatorial Pacific Ocean in March-April. This finding is consistent with the distribution of the tropospheric residual that has been derived previously which showed considerably more ozone over the tropical Atlantic than over the tropical Pacific.

E. No journal publications supported by these programs have been published yet.

A. Studies of Middle Atmospheric Radiative, Photochemical, and Dynamical Processes using Satellite Data

B. L. L. Hood (P.I.)  
S. W. Bougher (Co-I)  
Lunar and Planetary Laboratory  
University of Arizona  
Tucson, AZ 85721

C. Research Objectives

(i) Determine the response of middle atmospheric minor species and temperature to short-term solar ultraviolet variations occurring on the time scale of the solar rotation period; interpret the resulting measured responses theoretically.

(ii) Analyze existing satellite data sets covering the last solar cycle to estimate the primary chemical, thermal, and dynamical forcing of the middle atmosphere due to interannual solar ultraviolet variability.

(iii) Apply results of both the short-term and interannual data analyses in order to investigate secondary effects of solar ultraviolet variations on stratospheric dynamics and circulation, especially in the winter hemisphere. These secondary effects are of interest for obtaining a complete understanding of the solar cycle change in total ozone as well as for more accurately predicting the interannual climatology of the polar winter stratosphere.

D. Summary of Progress

(i) Measurements of short-term mesospheric ozone and temperature response amplitudes (defined as the percent change for a 1% change in the solar flux at a given wavelength such as Lyman  $\alpha$ ) and phase lags were obtained from an analysis of 3.8 years of SME IR ozone data and 4.3 years of Nimbus 7 SAMS temperature data. In agreement with at least one earlier study, the maximum low-latitude ozone and temperature response amplitudes occur at essentially the same level ( $\sim 0.06$  mbar; approximately 68 km altitude). The ozone response is negative and occurs at nearly zero lag while the peak temperature response is positive and occurs at a lag of 3 to 5 days (see the figure). The coexistence of positive temperature and negative ozone response maxima at the same level indicates strong coupling between photochemical and radiative components of the response. The negative ozone response can potentially be explained by a combination of temperature feedback from the observed temperature response and increased Lyman  $\alpha$  dissociation of water vapor (followed by  $\text{HO}_x$  destruction of ozone). The observed positive temperature response can not be due to ozone radiative heating since the ozone response is negative. However, other heating terms, including those due to exothermic chemical reactions, may be important. In particular,  $\text{HO}_x$  chemical heating (mainly from  $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$ ) will increase with ozone destruction and may therefore represent a likely candidate mechanism. Thus, further investigation of the mesospheric response to solar Lyman  $\alpha$  variations may provide a test of mesospheric heat budget models.

(ii) During the last year, we have published evidence that the upper stratospheric response to solar ultraviolet variations contains a dynamical component in addition to photochemical and thermal components. The evidence consists primarily of spectral co-

herencies at periods near 27 and 13 days between low-latitude average Nimbus 7 SAMS temperature deviations and higher-latitude temperature fluctuations of opposite sign in the winter hemisphere. Latitudinal temperature oscillations of this type result from interference between stationary and traveling wave components at stratospheric heights. It is therefore hypothesized that solar ultraviolet variations may force or modulate traveling waves with periods near 27 and 13 days in the upper stratosphere.

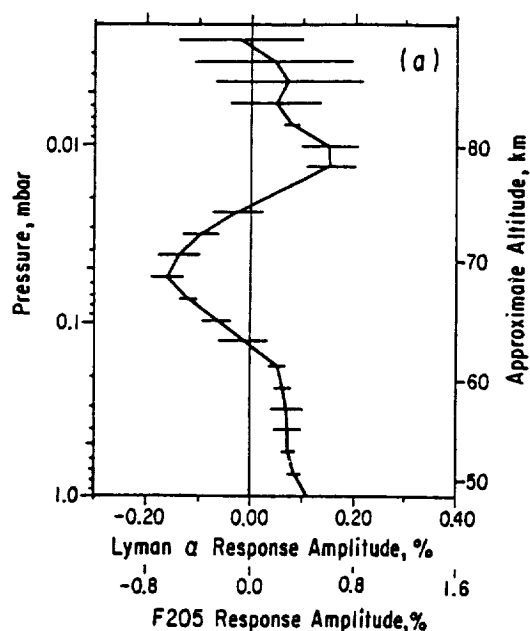
(iii) Recent studies of NMC/CAC temperature data for the period Oct. 1978 to Dec. 1988 suggest a possible solar cycle variation of temperature at low latitudes near the stratopause. Because of intercalibration uncertainties between the different satellite-borne instruments used to compile this data set (as well as the short data record) we regard this result as provisional. Further studies of contemporaneous satellite ozone records are in progress. The location of the derived variation is in accord with model predictions but the amplitude is larger than expected according to simple radiative photochemical models combined with the currently estimated solar cycle change in solar spectral irradiance (about 6 to 8% between 1980 and 1985).

#### E. Journal Publications in 1990 and 1991

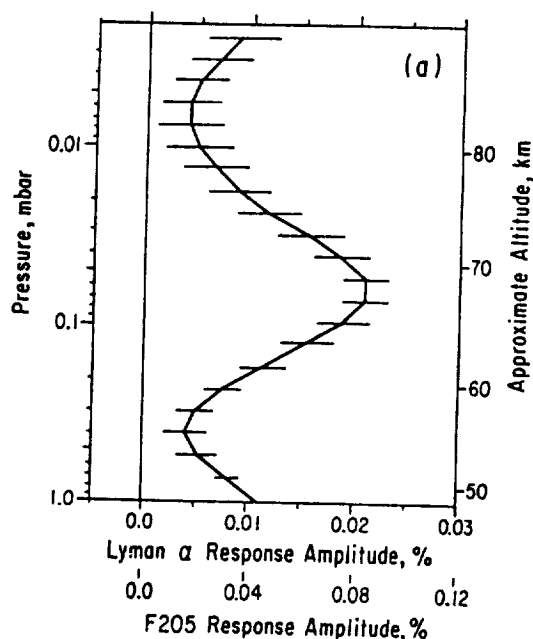
1. Hood, L. L. and J. L. Jirikowic, Stratospheric dynamical effects of solar ultraviolet variations: Evidence from zonal mean ozone and temperature data, *J. Geophys. Res.*, **96**, 7565-7577, 1991.

2. Hood, L. L., Z. Huang, and S. W. Bougher, Mesospheric effects of solar ultraviolet variations: Further analysis of SME IR ozone and Nimbus 7 SAMS temperature data, *J. Geophys. Res.*, **96**, 12989-13002, 1991.

#### SME IR Ozone



#### SAMS Temperature



**A. Title of Research Task:**

Analysis of Polar Stratospheric Cloud Formation Mechanisms

**B. Investigators and Institutions:**

Dr. Patrick Hamill  
Physics Department  
San Jose State University  
San Jose, California 95192

**C. Abstract of Research Objectives:**

The research project is a theoretical study of the formation and growth of polar stratospheric cloud particles. The study is specifically aimed at determining the nucleation process for polar stratospheric clouds (PSC's), the composition of the PSC particles, the morphology of the particles, the growth of the clouds due to condensation and coagulation, the sedimentation of the cloud particles, and the denitrification of the stratosphere by PSC particles. The work is based on theoretical studies of the type used to develop stratospheric background sulfate aerosol models. Verification of results is made by comparison with satellite and aircraft measurements.

**D. Summary of Progress and Results:**

The work has been progressing as expected. We have carried out studies in all of the areas mentioned above except for the morphology of growing PSC particles, which we expect to do this year. Much of the work done to date is summarized in a review article entitled "The Physics of Polar Stratospheric Clouds and the Ozone Hole" by Patrick Hamill and O. B. Toon which has been submitted for publication in Physics Today. We have also recently developed algorithms for determining the growth and evaporation of the PSC particles as well as their composition as a function of temperature. The results of the study are contained in a paper entitled "On the Growth and Evaporation of Nitric Acid Particles under Stratospheric Conditions". This paper has been submitted for publication in Nature. Some of our results concerning the nucleation of particles in the stratosphere, and on the sedimentation of the clouds and denitrification of the stratosphere are described in the journal publications listed in the next section.

An interesting new result obtained in collaboration with R. P. Turco of UCLA is the fact that reactions on the surfaces of supercooled stratospheric sulfate particles may be able to convert a significant amount of chlorine nitrate into HOCl. This result was presented at the IUGG meeting in Vienna in August, 1991 and a journal article is under preparation. This study also shows that considerable repartitioning of chlorine nitrate into a more reactive form may take place after large volcanic eruptions such as Pinatubo.

We have participated in various conferences and workshops including HSRP workshops at NASA Ames and at Virginia Beach. We edited a portion of the proceedings of the International Workshop on Stratospheric Aerosols: Measurements, Properties and Effects, held at AMES on March 27-30, 1990. We presented a paper at the 15th International Laser Radar Conference in July, 1990 at Tomsk, USSR in which we showed that new stratospheric aerosol particles are nucleated when the temperature drops during the early winter in the polar regions, but that this will not lead to an identifiable signal in lidar returns. This is due to the extremely small size of the newly formed particles.

In summary, the work carried out in 1990 and 1991 has led to a number of interesting results which have been presented to the scientific community in the form of oral presentations and journal articles.

#### **E. Journal Publications:**

- Hamill, Patrick, O. B. Toon and R. P. Turco, Aerosol nucleation in the winter Arctic and Antarctic stratospheres. Geophys. Res. Lett., 17, 417-420, 1990.
- Hamill, Patrick and O. B. Toon, Denitrification of the polar winter stratosphere: Implications of SAM II cloud formation temperatures. Geophys. Res. Lett., 17, 441-444, 1990.
- Elliott, S., R. P. Turco, O.B. Toon and Patrick Hamill, Incorporation of stratospheric acids into water ice. Geophys. Res. Lett., 17, 425-428, 1990.
- Jensen, Eric J., Owen B. Toon and Patrick Hamill, Homogeneous freezing nucleation of stratospheric solution droplets. In press, Geophys. Res. Lett., 1991.
- Pueschel, R. F., K. G. Snetsinger, P. Hamill, J. G. Goodman and M. P. McCormick, Nitric acid in polar stratospheric clouds: Similar temperature of nitric acid condensation and cloud formation. Geophys. Res. Lett., 17, 429-434, 1990.
- Toon, Owen B., R. P. Turco and P. Hamill, Denitrification mechanisms in the polar stratospheres. Geophys. Res. Lett., 17, 445-448, 1990.



## Stratospheric Temperature Trends

Years 1 & 2  
Years 3

PI: Robert Hudson  
PI: Paul Newman  
Code 916  
NASA/GSFC  
Greenbelt, MD 20771

CoIs: Mark R. Schoeberl

### Abstract

This investigation was an attempt to quantify temperature trends in the stratosphere. It is based upon the premise that Microwave Sounding Unit data can be used to assess temperature trends much more accurately than the conventional ground based radiosonde or rocketsonde data.

### Summary of Progress and Results

NMC monthly averages data from late 1978 to 1988, UKMO gridded analyses of TOVS data, and monthly averaged radiosondes constitute a long-term data bases for climatological studies. These data sets have been used for assessing future flight missions (e.g. SWAP and AASE II), while aiding in the analysis of past missions (e.g. AASE). They have been used in the analysis of stratospheric perturbations of the stratosphere, and are currently being used for studying the breakup of the Antarctic polar vortex.

The primary accomplishments over the course of this proposal has involved software development for unpacking, organizing, preprocessing, and analyzing gridded TIROS Operational Vertical Sounder (TOVS) data provided by the United Kingdom Meteorological Office (UKMO). The TOVS data include the High Resolution Infrared Sounder (HIRS), Microwave Sounding Unit (MSU), and Stratospheric Sounding Unit (SSU) instrument data.

The UKMO gridded TOVS data have many gaps, especially early in the 1978-1988 period. We linearly interpolated the daily data across a maximum gap of eight days. Monthly averages for each channel and grid point were then computed (a minimum of 20 days). Unfortunately, the data gaps in the UKMO gridded data forced us to regenerate the gridded data from the raw satellite data tapes available from the National Space Science Data Center (NSSDC). This NSSDC data set is complete from November 1978 to May 1985 (much more complete than that obtained from the UKMO), albeit with few available days. Over the last 8 months fortran software has been written to unpack these raw data tapes into brightness temperatures.

In addition to these trend tasks, support was provide to other studies requiring meteorological and climatological analyses. Among those studies were: climatological studies of the Northern Hemisphere winter during 1989, meteorological analysis of stratospheric lidar observations, and climatological and meteorological support for analysis of balloon borne observations.

### Publications 1990-1991:

1. "Lidar Observations of Ozone Changes Induced by Air Mass Motions," T. J. McGee, R. Ferrare, J. Butler, P. Newman, D. Whiteman, J. Burris, S. Godin, and I. S. McDermid, *J. Geophys. Res.*, **95**, 20527-20530, 1990.

2. "Stratospheric Temperatures During the 88-89 Northern Hemisphere Winter," Paul A. Newman, Leslie R. Lait, Mark R. Schoeberl, and Ronald M. Nagatani, *Geophys. Res. Lett.*, **17**, 329-332, 1990.
3. "A Comparison of Arctic Lower Stratospheric Winter Temperatures for 1988-89 with Temperatures Since 1964," R. M. Nagatani, A. J. Miller, M. E. Gelman, and P. A. Newman, *Geophys. Res. Lett.*, **17**, 333-336, 1990.
4. "Comparison of Ozone Profiles from Ground-Based Lidar, ECC Balloon Sonde, ROCOZ-A Rocketsonde, and SAGE II Satellite Measurements," I. S. McDermid, R. A. Barnes, C. L. Parsons, A. Torres, M. P. McCormick, W. P. Chu, P. Wang, J. Butler, P. Newman, J. Burris, R. Ferrare, D. Whiteman, and T. J. McGee, *J. Geophys. Res.* (in press), 1990.
5. "Depletion of Arctic Ozone in the Winter 1990," M. Koike, Y. Kondo, M. Hayashi, Y. Iwasaka, P. A. Newman, M. Helten, P. Amedieu, *Geophys. Res. Lett.*, **18**, 791-794, 1991.
6. "Seasonal and Longitudinal Variations in Tropical Total Ozone and the Tropopause," P. D. Guthrie, P. A. Newman, R. S. Stolarski, *Geophys. Res. Lett.*, (submitted), 1991.
7. "Reactive Nitrogen, Ozone, and Nitrate Aerosols Observed in the Arctic Stratosphere in January 1990," Y. Kondo, P. Amedieu, M. Koike, Y. Iwasaka, P. A. Newman, U. Schmidt, and W. A. Matthews, *J. Geophys. Res.* (submitted), 1991.
8. "An Investigation into the Reduction of Stratospheric Ozone in the Southern Australasian Region," P. Lehmann, D. J. Karoly, P. A. Newman, T. S. Clarkson, and W. A. Matthews, *Nature* (submitted), 1991.
9. "STROZ LITE: Goddard's Stratospheric Ozone Lidar Trailer Experiment," T. McGee, R. Ferrare, J. Butler, P. Newman, D. Whiteman, and J. Burris, *NASA Tech Memo*, 1990.

A. "Direct Measurements of Tropospheric Ozone from TOMS Data"

B. Robert D. Hudson, University of Maryland at College Park

C. Abstract of Research Objectives

Measurements of the global tropospheric ozone field are of great importance for a full understanding of the chemical and dynamical processes that control the distribution and amount of trace gases in the troposphere and stratosphere. In preliminary work it has been shown that absolute tropospheric ozone amounts can be derived directly from the radiance data of the Total Ozone Mapping Spectrometer. The method involves the inversion of the ratio of the measured albedos at a pair of wavelengths, at two near contiguous points on the earth, one measurement being over a region of high reflectivity, e.g., clouds or snow/ice, the other over a region of low reflectivity, e.g., soil/sea surface. The ozone amount retrieved is either that between the cloud top and the ground, or between the tropopause and the ground. The expected accuracy of the method is between 3 and 4 Dobson Units (DU) for the present TOMS, but should be better for the planned TOMS instruments.

D. Summary of Progress and Results

This task was initiated in September 1991. Since then a preliminary analysis of the method has been carried out, with particular emphasis on the expected accuracy of the method. For the cloud/non-cloud case, the expected accuracy is between 3 and 4 Dobson Units, compared to typical tropospheric ozone amounts of 20 to 50 Dobson Units. The largest source of error is the digitization error of the TOMS electrometer which returns a seven bit word. In future TOMS instruments this error will be reduced considerably (at least a nine bit word is returned). Other sources of error are the determination of the height of the clouds (2 DU), and the reflectivity of the lower boundary (1 DU). The International Satellite Cloud Climatology Project cloud data sets have been obtained and will be used to derive cloud heights. Finally, the TOMS High Density Data Set for selected years has been obtained from the NSSDC.

E. None

A Research Summary to  
National Aeronautics and Space Administration

**Title:** Perturbations and Trends in the Middle Atmosphere

**Principal Investigator:** Gerald M. Keating  
NASA Langley Research Center  
Hampton, VA 23665-5225

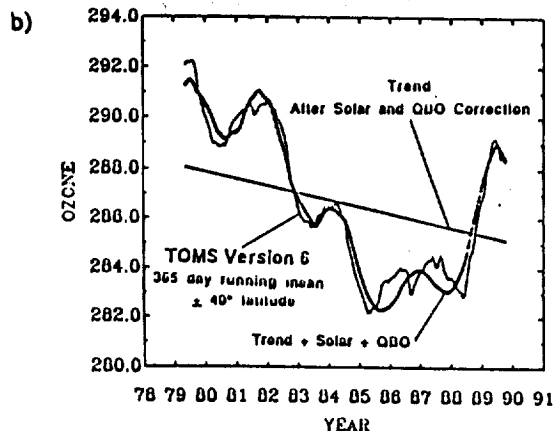
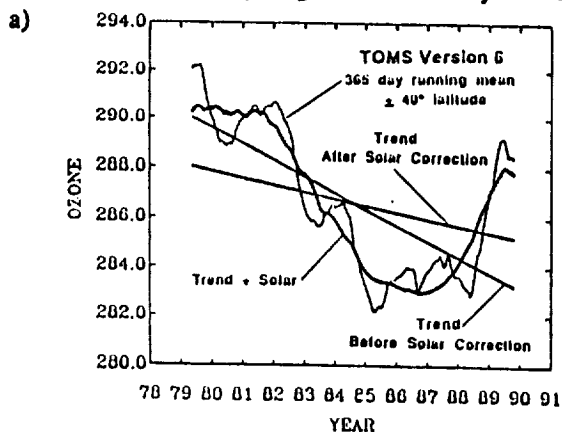
**Co-Investigator:** G. Brasseur, NCAR, Boulder, CO

**Abstract of Research and Objectives:** (1) Using various satellite data sets, determine to good statistical accuracy the response of stratospheric and mesospheric minor species and temperature to 27-day solar UV variations and interpret results; (2) Estimate the response to 11-year solar UV variations taking into account the observed 27-day response and the longer response times; (3) Using long-term data sets, correct for estimated 11-year variations and isolate long-term trends; and (4) Develop improved climatologies for ozone.

**Summary of Progress and Results:**

We have detected the response of total column ozone to short-term solar UV variations. Latitudinal-seasonal variations in the amplitude and phase of response have been isolated. Minimum response times occur in the summer hemisphere and maximum amplitude of response occurs in the winter hemisphere. A major unexpected result is that the observed response per unit change in UV is much stronger (by factor of 2) than indicated by the Brasseur et al. 1D or 2D models.

An approach was developed and tested to use the statistically significant results on the response of total column ozone to 27-day solar UV variations to estimate the 11-year variations after adjusting for the theoretical difference in sensitivity between short-term and long-term responses. By properly correcting for solar effects long-term trends were then isolated. Based on 11 years of the newly archived TOMS version 6 total column ozone data between  $\pm 40^\circ$  latitude, the estimated ozone/UV response, and 11 years of the Mg II core-to-wing ratio solar UV index, observations were compared with predictions. Ignoring the 11-year solar effect resulted in a trend estimate of a 2% decrease in ozone within  $40^\circ$  of the equator over the 1980's. Properly including the 11-year solar effect (2% ozone variation) reduced the trend estimate by a factor of 2 (Figure a). Including the QBO reduced the standard deviation in predictions of the 365-day running mean from 2.2 Dobson Units to 0.5 Dobson Units but didn't significantly alter the trend estimate (Figure b). It is clear that the 11-year variation must be removed to accurately detect trends and that the statistically significant 27-day variation should be used in the 11-year estimate.



Near the equatorial stratopause, the amplitude of the temperature response to a one percent change in UV index is predicted to be nearly the same on the 27-day and 11-year time scales. We tested this hypothesis by comparing the statistically significant observed 27-day temperature/UV response with the long-term response based on 11 years of NOAA satellite measurements. We found that the short-term response could be used to estimate the long-term solar effect. Equatorial temperatures at 2 mb apparently decreased about 1.6 K during the 1980's with a superimposed 1 K long-term solar effect. The trend determination was found to be strongly coupled to the 11-year solar effect.

Previously we discovered two important phenomena in the equatorial mesosphere. The decrease of ozone near 70 km responding to cyclic increases in solar Lyman alpha, and the corresponding strong increases in temperature at these altitudes with solar increases. Both of these phenomena have recently been confirmed by other investigators. Our studies now show that both of these phenomena are global in nature. We attributed the ozone decrease to  $\text{Ly}\alpha$  dissociation of water vapor producing  $\text{HO}_x$  which could act as a catalyst for ozone depletion. A recent collaborative theoretical study with Summers et al, which assumed this process, gave results consistent with our observations and showed the dependence of the ozone response on  $k_{zz}$  and  $\text{H}_2\text{O}$  vapor vertical structure.

From a collaborative study, using the Brasseur et al. 2D model, it is found that the unexpectedly long response times of stratospheric temperatures to 27-day solar UV variations can be explained in terms of adiabatic heating/cooling of air parcels.

The P.I. is now Chairperson of STEP Project 5.2 on the atmospheric response to short-term solar variations and Chairman of the COSPAR Task Group for Volume 3 of CIRA (Trace Species Climatologies). In the latter capacity he is generating an international reference atmosphere for ozone based on 5 satellite experiments. Recent improvements include tables of global diurnal variations in mesospheric ozone and extensions in monthly latitudinal tables down to the tropical tropopause.

### Publications

- Keating, G. M. and C. Chen, Middle atmosphere change through solar forcing, Adv. Space Res., 11, #3, 9, 1991.
- Rycroft, M. J., G. M. Keating and D. Rees (Editors): Upper Atmosphere Models and Research, Adv. Space Res., 10, #6, 1990, 307 pages (Pergamon Press, Oxford).
- Summers, M. E., et al. (including G. M. Keating): A model study of the response of mesospheric ozone to short-term solar ultraviolet flux variations, J. Geophys. Res., 95, 22,523, 1990.
- Keating, G. M., C. Chen, and M. Hitchman: Recent results on response of middle atmosphere to short-term solar UV variation, Annales Geophysicae, 1990 Special Issue, 258, 1990.
- Keating, G. M. (Editor): Reference Models of Trace Species, MAP Handbook 31 (Published in 1991), 180 pages.
- Keating, G. M., M. C. Pitts, and D. F. Young: Ozone reference models for the middle atmosphere, Chapter 15, CIRA Part II (Middle Atmosphere Models), Adv. Space Res., 10, #12, 317, 1990.
- Keating, G. M., C. Chen, and M. C. Pitts: Improved reference models for middle atmosphere ozone, Adv. Space Res., 6, 37, 1990.
- Keating, G. M. and C. Chen: Extensions to the CIRA reference models for middle atmosphere ozone, Adv. Space Res. (accepted for publication), 1991.
- Keating, G. M., G. Brasseur, N. C. Hsu, L. S. Chiou, and M. Gelman: The influence of solar UV variability on the middle atmosphere, Annales Geophysicae, 9, 274, 1991.

## RESEARCH SUMMARY

### A. TOMS Data Analysis

### B. Arlin J. Krueger

Code 916

Goddard Space Flight Center

Greenbelt, MD 20771

C. This research is directed to observing and analysing polar and global ozone changes with the Total Ozone Mapping Spectrometer (TOMS) instruments on the Nimbus 7 and Meteor-3 spacecraft. During special periods of interest, such as during the formation of the Antarctic ozone hole, the TOMS data are processed in near real time for timely analysis and delivery to research scientists in the Antarctic to aid in scheduling and interpretation of their measurements. Reports on the status of Antarctic ozone are made available to the scientific community and to the public. In addition, the state of Arctic ozone is monitored for indications of significant depletion.

D. The development of the Antarctic ozone hole was tracked from near real time processing of TOMS observations made in August through December 1990 and August - November 1991 as has been done each year since 1987. The contoured ozone data were transferred within 24 hours to the NSF Antarctic Support organization for delivery to McMurdo Station and other location of Antarctic research programs. In 1991 the contoured data were transmitted to the National Institute for Polar Research in Japan for their use in planning an Antarctic circumpolar balloon flight with instruments to detect chemical species important to ozone depletion. Special analyses of TOMS ozone over the Pacific Ocean were also delivered to Guam and Tokyo for use in investigation of the low ozone regions in the tropics during the Pem-West Experiment.

The depth and size of the Antarctic ozone hole varied with a two year cycle during the 1980 decade. The maximum depletion was found in odd-numbered years such as 1987 when record low ozone values were observed. With weak depletion found in 1988, it was expected that 1990 would produce a similar weak depletion. However, the two year cycle was interrupted. It was found that ozone depletion began earlier than in 1989 and the depth and area of the ozone hole was equal to the record year of 1987. This behavior is attributed to increasing amounts of CFC's in the atmosphere, producing higher ClO concentrations in the polar spring and to a change in the polar atmosphere circulation during southern hemisphere winter.

In 1991 the ozone hole again began to form in late August and continued to deepen at a rate similar to 1989 and 1990. The deepening accelerated in mid September to produce record low ozone values. Thus the last three years have produced deep ozone holes similar to the record-breaking 1987 ozone hole.

### E. Publications:

P. Newman, R. Stolarski, M. Schoeberl, R. McPeters, and A. Krueger, "The 1990 Antarctic ozone hole as observed by TOMS", *Geophys. Res. Lett.*, 18, 661-661, 1991.

A. J. Krueger, L. M. Penn, P. T. Guimaraes, C. J. Scott, D. E. Larko, and S. D. Doiron, "Nimbus-7 TOMS Antarctic ozone atlas: August through December 1990", *NASA Ref. Publ.* 1264, June 1991.

R. S. Stolarski, M. R. Schoeberl, P. A. Newman, R. D. McPeters, and A. J. Krueger, "The 1989 Antarctic ozone hole as observed by TOMS", *Geophys. Res. Lett.*, 17, 1267-1270, 1990.

Theoretical Studies of Stratospheric Chemistry : NAGW-1230

Principal Investigators : Michael B. McElroy and Steven C. Wofsy

Co-Investigator : Ross J. Salawitch

Harvard University

*Abstract of Research Objectives.* Our program of research is designed to investigate factors that influence the chemical composition of the stratosphere. Our work is motivated by concerns that anthropogenic activities have modified and may further modify the abundance of stratospheric ozone.

*Summary of Progress and Results.* Our research during the past two years has involved assimilation of chemical and meteorological data collected during the Arctic Airborne Stratospheric Experiment (AASE) and theoretical investigations into the behavior of polar stratospheric clouds (PSCs). Analysis of the AASE data, collected during the winter of 1989-90, was designed to quantify the loss of  $O_3$  over the course of the mission and to better understand the processes responsible for the highly perturbed chemistry typical of the springtime polar stratospheres. Studies of PSCs address the microphysical processes responsible for the observed denitrification of the polar stratosphere during winter.

Assessment of the time integrated loss of  $O_3$  during AASE required significant extrapolation from *in situ* observations, since the chemically perturbed polar vortex was sampled in limited geographic regions that generally received less solar illumination (a necessary ingredient for loss of  $O_3$ ) than the rest of the vortex. A photochemical model and observed fields of potential temperature and potential vorticity were used to extrapolate *in situ* measurements of ClO and BrO to larger regions of the vortex. The calculated loss of  $O_3$  was estimated to be 12% for the range of altitudes sampled *in situ* by the ER-2 aircraft during AASE, in agreement with observed rates for removal of  $O_3$ . About 60% of the loss of  $O_3$  was attributed to the ClO-ClO mechanism with the remainder due to the BrO-ClO cycle.

The column abundance of a variety of chlorine and nitrogen bearing species was measured from the DC-8 aircraft employed during AASE. We have developed a model that uses observed fields of potential vorticity and potential temperature combined with empirical relationships from mid-latitude regions between chemical tracers and meteorological fields to reconstruct profiles (and hence column abundances) for gases whose distribution in the high latitude regions during winter is determined primarily by transport (gases that are characterized by long chemical lifetimes in the absence of heterogeneous processes). Departures from conservative behavior for total  $NO_y$ , total  $Cl_x$ , HCl, and  $ClNO_3$  have been interpreted to infer the following effects of heterogeneous processing during the course of AASE : conversion of  $NO_x$  to  $HNO_3$ , condensation of  $HNO_3$ , conversion of HCl to  $ClNO_3$ , and conversion of HCl and  $ClNO_3$  to species not measured from the DC-8 (presumably ClO and  $Cl_2O_2$ ). Analysis of measurements of HF led to the suggestion of heterogeneous conversion of  $COF_2$  to HF on the surface of PSCs.

Removal of  $HNO_3$  (denitrification) is a key feature of the perturbed chemical environment leading to accelerated loss of  $O_3$  for the springtime polar stratosphere, although the specific mechanism for removal of  $HNO_3$  is uncertain. We have developed microphysical models to simulate the growth of PSCs as nitric acid trihydrate (NAT) condenses on background

stratospheric aerosols. We found that cooling rates less than  $0.5$  to  $1.0 \text{ K day}^{-1}$  lead to differential growth of NAT particles that are large enough to fall appreciable distances on time scales close to one week, which may account for denitrification of the inner vortex. We suggested that rapid cooling rates may lead to accretion of a coating of NAT on ice particles falling from above that inhibits subsequent evaporation of the ice nuclei. This mechanism provides an efficient mechanism for irreversible removal of  $\text{HNO}_3$  from outer regions of the vortex and may account for the puzzling observation of large particles, presumably composed of mainly ice, in air with temperatures above the frost point. Both mechanisms for denitrification are consistent with observations of denitrification with little or no dehydration.

Our current research is focussed on the following topics:

- Development of a compact quantum mechanical model, using recent high resolution data for line strengths and widths of  $\text{O}_2$ , for accurate calculation of atmospheric transmission of radiation in the Schumann-Runge region of  $\text{O}_2$ . Radiation in this region plays an important role in the production of odd oxygen for altitudes greater than  $50 \text{ km}$  and in regulating the vertical distribution of  $\text{NO}_y$  and  $\text{Cl}_x$ .
- Use of photochemical models and reconstruction techniques based on chemical and meteorological data to estimate loss of  $\text{O}_3$  in the entire column of the polar vortex during AASE, including altitudes inaccessible to the ER-2. Loss of  $\text{O}_3$  will be estimated for perturbed air subsequent to the end of AASE, and the contribution of chemically perturbed air from the polar region to the observed decline of  $\text{O}_3$  in northern mid-latitudes in early spring will be determined.
- Evaluation of the role of heterogeneous processes on the global  $\text{O}_3$  balance by comprehensive analysis of existing data for key radical and reservoir species of the oxides of nitrogen, hydrogen, and chlorine (ATMOS, LIMS, SAGE, balloon soundings). The importance of heterogeneous reactions occurring on the surface of background sulfate aerosols will be determined, and model calculations will be used to aid planning and analysis of data for pending field missions.

#### *Journal Publications*

- Salawitch, R. J., M. B. McElroy, J. H. Yatteau, S. C. Wofsy, M. R. Schoeberl, L. R. Lait, P. A. Newman, K. R. Chan, M. Loewenstein, J. R. Podolske, S. E. Strahan, and M. H. Proffitt, Loss of ozone in the Arctic vortex for the winter of 1989, *Geophys. Res. Lett.*, **17**, 561–564, 1990.
- Wofsy, S. C., G. P. Gobbi, R. J. Salawitch and M. B. McElroy, Nucleation and growth of  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$  particles in the polar stratosphere, *J. Atmos. Sci.*, **47**, 2004–2012, 1990.
- Wofsy, S. C., R. J. Salawitch, J. H. Yatteau, M. B. McElroy, B. W. Gandrud, J. E. Dye, and D. Baumgardner, Condensation of  $\text{HNO}_3$  on falling ice particles: mechanism for denitrification of the polar stratosphere, *Geophys. Res. Lett.*, **17**, 449–452, 1990.
- Wofsy, S. C., J. H. Yatteau, R. J. Salawitch, M. B. McElroy, G. C. Toon, W. B. Mankin and M. T. Coffey, Heterogeneous conversion of  $\text{COF}_2$  to HF in polar stratospheric clouds, *Geophys. Res. Lett.*, **17**, 461–464, 1990.
- Yatteau, J. H., S. C. Wofsy, R. J. Salawitch, M. B. McElroy, M. R. Schoeberl, L. R. Lait, P. A. Newman, A. Torres, T. Jorgensen, W. G. Mankin, M. T. Coffey, G. C. Toon, M. Loewenstein, J. R. Podolske, S. E. Strahan, K. R. Chan, and M. H. Proffitt, Effects of transport on column abundances of nitrogen and chlorine compounds in the Arctic stratosphere, *Geophys. Res. Lett.*, **17**, 533–536, 1990.



- A. Satellite Data and the UV Spectra of the Atmosphere  
old UPN: 673-41-45  
new UPN: 579-21-43
- B. Dr. Richard D. McPeters  
NASA / Goddard Space Flight Center
- C. Research Objectives:

This task supports work to understand details of the UV radiation field in the atmosphere that will aid in achieving the high accuracy needed to measure ozone trends using SBUV/TOMS type instruments. The research uses spectral scan data from these instruments in addition to operational data to evaluate specific atmospheric effects. Areas of study include the effect of profile shape on ozone retrievals at high zenith angles, the effect of possible mesospheric clouds, the effect of aerosols on the backscattered albedo, and the measurability of non-ozone constituents such as nitric oxide and sulfur dioxide.

D. Summary of Progress and Results

Work was done last year in cooperation with Dr. Gary Thomas at the University of Colorado in which albedo anomalies in the SBUV data were identified as being caused by scattering from polar mesospheric clouds. The annual formation of PMCs in the summer polar cap region seen in the SME data has now been seen in the shortest wavelength channels of the SBUV and SBUV/2 instruments. The location, timing, and wavelength signature of the anomalous albedo perturbations seen in SBUV data have been shown to be consistent with their being caused by PMCs. Examination of the long term SBUV record shows that the frequency of occurrence of PMCs increased between 1978 and 1986, supporting an anticorrelation of PMCs with solar cycle.

This task also supported work on the "day 1 calibration" question. Immediately after launch instruments that have been calibrated in the laboratory with the greatest possible accuracy produce total ozone amounts from the different wavelength pairs that are inconsistent. For SBUV, the B pair ozone is consistently 2% higher than the A pair ozone, while the C pair ozone is 10% lower than A. We have examined the question of whether these differences are caused by ozone cross section errors or by calibration errors or whether there are consistencies that suggest that they are caused by subtle radiative transfer errors such as profile shape effects, varying sensitivity to tropospheric ozone, or errors due to cloud height uncertainty. The initial conclusion is that most of the error is caused by the limitations with which ground calibration can be done. But there are some consistencies across instruments that suggest that a small part of the error is caused by cross section error or by radiative transfer effects.

E. Journal Publications

"Long-term Changes in SBUV/TOMS Relative to World Primary Standard Dobson Spectrometer 83," McPeters, R.D. and W.D. Komhyr, *J. Geophys. Res.*, **96**, 2987-2994, 1991.

"Satellite Observations of Polar Mesospheric Clouds by the SBUV Spectral Radiometer: Evidence of a Solar Cycle Dependence," G.E. Thomas, R.D. McPeters, and E.J. Jensen, *J. Geophys. Res.*, **96**, 927-939, 1991.

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"Total Ozone Trends Deduced from Nimbus 7 TOMS Data," R. S. Stolarski, P. Bloomfield, R. McPeters, and J. Herman, *Geophys. Res. Lett.*, **18**, 1015-1018, 1991.

# **A STUDY OF THE AEROSOL EFFECT ON UMKEHR OZONE PROFILES USING SAGE II DATA**

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## **ABSTRACT**

This study examines 1299 coincidences of SAGE II and Umkehr ozone profiles within 1000 km and 12 hours between October 1984 and April 1989. A comparison of layer ozone amounts indicates less than 10% average ozone difference in layers 5 through 9, SAGE II 15-30% higher in layer 4, and 31% higher, on average, in layer 3. Large variations exist among stations in all layers. Cross correlations of SAGE II ozone and aerosol amounts, by layer, suggest that these parameters are not independent. The aerosol effect on the layer ozone differences in layers 7, 8, and 9 is less than 2% per 0.01 stratospheric aerosol optical depth; however, the optical depths are extremely small.

## **PROGRESS AND RESULTS**

The database for this research derives from version 5.5 of the SAGE II satellite measurements between November 1984 and April 1989. Each processed event includes stratospheric aerosol optical depths at four measured and one extrapolated (Umkehr) wavelength; profiles (at approximately 1-km intervals on standard Umkehr pressure surfaces) of ozone, temperature, NO<sub>2</sub>, H<sub>2</sub>O, Rayleigh extinction at seven wavelengths, and aerosol extinction at five wavelengths; and 380 words of housekeeping data. Additionally, the database includes all Umkehr observations that occurred within 4000 km, 30 hours, and 10° latitude of a SAGE II measurement. These coincidence criteria result in approximately 10,000 SAGE II-Umkehr cases.

Preliminary statistical analysis of this database produced univariate statistics (mean, variance, histograms, etc.) of the difference between the SAGE II and Umkehr ozone measurements in Umkehr layers 3 through 9, the distance between satellite and ground instruments, time difference, latitude difference, stratospheric aerosol optical depth at three wavelengths (1.02, 0.525, and 0.32 microns), season, total column ozone, troposphere height, and Umkehr station. As part of a data-sanity check, univariate statistics (comprising 10,000 pages) of the housekeeping data were also calculated.

In order to address the central thesis of this study, I produced a subset of the 10,000-case database that includes only coincidences within 1000 km and 12 hours. That

restriction results in 1299 cases representing 19 Umkehr stations over the 4.5-year study period. With this smaller data set, I calculated percentage ozone differences in layers 3 through 9 for all Umkehr stations with more than 9 SAGE II coincidences; the aerosol effect on these ozone differences separated by station and layer; and finally, the significant correlations of the ozone differences with other parameters (e.g., total ozone, tropopause height, season, and layer ozone amounts).

The case study reveals that the average (SAGE II-Umkehr)/Umkehr percentage ozone differences are less than 10% in layers 5 through 9, with large differences at some stations. In layer 4, SAGE II is typically 15-20% higher, except at a few stations. Differences in layer 3 show SAGE II 31% higher, on average, with sizable variation among stations.

Cross correlations of SAGE II layer ozone, Umkehr layer ozone, within-layer ozone differences, SAGE II layer aerosol, and tropopause height indicate strong associations between adjacent layer ozone and ozone difference, as well as significant correlations between SAGE II ozone and SAGE II aerosol amounts in layers 3 through 7. Additionally, stepwise regression analysis shows that the total stratospheric optical depth is a poor predictor of layer ozone difference between SAGE II and Umkehr.

The average aerosol effect on ozone differences in layers 7, 8, and 9 is less than 2% per 0.01 stratospheric aerosol optical depth at 0.525 microns. Because of the low stratospheric aerosol loading during the study period, this result can not be applied to the effect experienced during the El Chichon or Mt. Pinatubo periods when the aerosol loadings are much higher.

## PUBLICATIONS

Newchurch, M.J., G.W. Grams, D.M. Cunnold, and J.J. DeLuisi, 1988: A comparison of SAGE I and Umkehr ozone profiles including a search for Umkehr aerosol effects, *Proceedings of the Quadrennial Ozone Symposium*, Gottingen, Federal Republic of Germany, 8-13 August 1988.

Newchurch, M.J. and D.M. Cunnold, 1990: Comparison of SAGE II and Umkehr ozone profiles as functions of stratospheric optical depth, total ozone, season, and tropopause height, *Proceedings of the Topical Meeting on Optical Remote Sensing of the Atmosphere*, Optical Society of America, Lake Tahoe, NV, February 1990.

Newchurch, M.J. and D.M. Cunnold, Aerosol effect on Umkehr ozone profiles using SAGE II measurements prior to the Pinatubo eruption, in preparation for JGR.

A Research Summary to  
National Aeronautics and Space Administration

**Title of Research Task:** Statistical Analysis of Stratospheric Temperature and Ozone Profile Data for Trends and Model Comparisons

**Principal Investigators:** G. C. Reinsel, University of Wisconsin, Madison, and  
G. C. Tiao, University of Chicago

**Abstract of Research and Objectives**

The principal purpose of this research is to perform statistical analyses of worldwide temperature profile data and atmospheric total ozone and ozone profile data over the period 1960 to 1989, for the detection of trend. Our research efforts have been concentrated primarily in the following areas: (a) trend analysis of rawinsonde station temperature data and comparisons with model calculations; (b) trend analysis of NOAA satellite stratospheric temperature data; (c) update through 1989 of analysis of the effects of stratospheric aerosols on recent ground-based Umkehr ozone profile measurements and trend analysis of the aerosol-corrected Umkehr data; (d) update of time series analysis of ground-based Dobson total ozone data to investigate ozone trends over different seasons and solar cycle effects.

**Summary of Progress and Results**

**(a) Trend Analysis of Rawinsonde Temperature Data**

Trend analysis is performed for temperature profile data from a global network of 62 rawinsonde stations over the period 1964–1988. The rawinsonde temperature data consist of time series of monthly average temperatures at 10 pressure levels (surface, 850, 700, 500, 300, 200, 150, 100, 50, and 30 mb). Time series trend models were fitted to the data by maximum likelihood estimation for each of the 10 pressure levels and each station. For some pressure levels at several stations, especially surface level, a level shift intervention term was included in the trend model to account for an apparent shift in the mean level of the temperature data. The overall global trend results for the rawinsonde data show significant positive trends of the order of  $0.3^{\circ}\text{C}$  per decade in the surface to 500 mb altitude range, with trends then gradually decreasing to a significant negative value of about  $-0.3^{\circ}\text{C}$  per decade at 100 mb, and then becoming less negative above 100 mb. The empirical temperature trend results for the lower stratosphere are compared with changes in temperature determined from a radiative equilibrium model calculation that proscribes an ozone change over the altitude region, surface to 50 km, as determined empirically from separate trend analyses of ozonesonde and Umkehr ozone profile data. The empirical and calculated trends in lower stratospheric temperature indicate substantive agreement in profile shape and magnitude, although the rawinsonde data negative trends in the 15 to 20 km region are less negative than the model calculations.

**(b) Trend Analysis of NOAA Satellite Stratospheric Temperature Data**

A trend analysis of stratospheric temperature data from NOAA satellites is performed for the period October 1978 through December 1989. The data consist of monthly average temperatures measured at 7 pressure levels (70, 50, 30, 10, 5, 2 and 1 mb) for 36 latitude zones ( $0^{\circ}\text{N}$  to  $85^{\circ}\text{N}$  and  $0^{\circ}\text{S}$  to  $85^{\circ}\text{S}$  at  $5^{\circ}$  intervals). For this relatively short (11-year) time period, the trend results show generally negative trends of the order of  $-0.4^{\circ}\text{C}$  per decade in the region of 70 to 30 mb and positive trends at 10 mb, with no distinct pattern in the trends as a function of latitude. For the upper pressure levels of 5, 2 and 1 mb, the trend results have higher uncertainty and exhibit considerably more variation with latitude but no systematic patterns are apparent, and the overall trends are roughly near zero.

for 5 and 2 mb and somewhat negative at 1 mb.

(c) Update of Analysis of Recent Umkehr Data for Trends

Trend analysis of stratospheric Umkehr profile ozone data for Umkehr layers 3–9 (approximately 15 to 49 km) from 11 Northern Hemisphere Umkehr stations has been updated to cover the period 1977–1989. The correction method used in the analysis to adjust the Umkehr measurement data for errors caused by volcanic aerosols associated with El Chichon is the empirical method based on use of optical thickness time series data, similar to the method described in Reinsel et al. (1989). The optical thickness data consist of aerosol data obtained from the SAGE II satellite for the period Nov. 1984 through Oct. 1989 combined with the pre-1984 aerosol data derived from ground-based lidar data measurements. Linear trend models which also include the  $F_{10.7}$  solar flux term were estimated for each station using the empirical-model aerosol error correction method. The trend and solar cycle results indicate a significant overall negative trend, exclusive of trend variations associated with solar flux variations, of the order of  $-0.5\%$  per year in Umkehr layers 7–9 over the period 1977–1989, and a significant positive solar cycle association in all layers 3–9. Trend results in layers 5–9 for the period 1977–1989 are similar to previous results for 1977–1987 reported by Reinsel et al. (1989). However, the trend in layer 4 is somewhat more negative for the extended period ( $-0.30\%$  per year for 1977–1989 compared with  $-0.19\%$  per year for 1977–1987), and the trend estimate in layer 3 (15–19 km) for 1977–1989 was also significantly negative,  $-0.54 \pm 0.46\%$  per year.

(d) Seasonal Trend Analysis of Dobson Total Ozone Data

A seasonal trend analysis of Dobson total ozone data has been updated using published Dobson data through 1989 from 35 North Hemisphere stations located between  $18^\circ\text{N}$  and  $64^\circ\text{N}$  latitude. The seasonal trend model considered allows for a different trend for each month of the year to examine the seasonal nature of ozone trend behavior. The statistical model also includes an  $F_{10.7}$  solar flux term and a 50 mb equatorial wind QBO term. Using data for the entire period 1958–1989, the overall trend results indicate substantially more negative trends during the winter (December–March) months than during the summer (May–August) and fall (September–November) months, with overall winter, summer and fall trend estimates over all latitudes of the order of  $-1.7\%$ ,  $-0.3\%$  and  $-0.1\%$  per decade. The year-round or annual trend estimate, with associated 95% confidence limits, is  $-0.86 \pm 0.53\%$  per decade. The most negative trends in the published data occur in the  $39^\circ\text{N}$ – $50^\circ\text{N}$  latitude zone. The sensitivity of these seasonal trend results to the data period was also examined by performing a trend analysis using only more recent data for the period 1971–1989. The corresponding overall winter, summer and fall trend estimates were about  $-1.7\%$ ,  $-0.8\%$  and  $-1.0\%$  per decade, with year-round or annual trend estimate of  $-1.19 \pm 0.62\%$  per decade. Hence, using data for the more recent period 1971–1989, similar trends are found for the winter season compared to the data period 1958–1989, but trends are more negative for the summer and fall seasons over the period 1971–1989.

Journal Publications

- Bojkov, R., L. Bishop, W. J. Hill, G. C. Reinsel, and G. C. Tiao (1990). A statistical trend analysis of revised Dobson total ozone data over the northern hemisphere, *J. Geophys. Res.*, 95, 9785–9807.
- Miller, A. J., R. M. Nagatani, G. C. Tiao, X. F. Niu, G. C. Reinsel, D. Wuebbles, and K. Grant (1991). Comparisons of observed ozone and temperature trends in the lower stratosphere, submitted to *Geophys. Res. Lett.*.
- Reinsel, G. C., G. C. Tiao, J. J. DeLuise, S. Basu, and K. Carriere (1989). Trend analysis of aerosol-corrected Umkehr ozone profile data through 1987, *J. Geophys. Res.*, 94, 16,373–16,386.

Title: Analysis of Observations of the Middle Atmosphere from Satellites

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Abstract of Research and Objectives

Satellite data are being used to investigate problems in middle atmosphere chemistry and dynamics. Efforts have been focused primarily on studies to determine the quality of observed distributions of trace species and derived dynamical quantities. Those data have been used as diagnostics for model-derived constituent profiles and fields and for improving our understanding of some of the fundamental processes occurring in the middle atmosphere.

Summary of Progress and Results

The most widely used form of the Nimbus 7 LIMS data set, the LIMS Map Archival Tapes, or LAMAT, has been described in some detail. Its accuracy has been established by comparing zonal variances about daily zonal mean values, as also obtained from the original profile input data. Such variance information is useful for validating the amount of "wave activity" in 3-D model simulations of the middle atmosphere and as a first-guess climatology for satellite retrieval studies.

The quality of derived winds has been established by comparisons with in situ observations. Calculations using LIMS data reveal that use of balanced, rather than geostrophic, zonal and meridional wind components is also important for accurate estimates of the meridional eddy momentum flux. Errors in base-level heights present problems for dynamical calculations in the Southern Hemisphere. A compilation of sudden stratospheric warming events from many years of Stratospheric Sounding Unit (SSU) data shows that warmings evolve from very similar conditions on time scales of several weeks. Preferred states of the stratosphere have been found as noted by a bimodality in the frequency distribution of the wave-1 amplitudes.

The importance of non-LTE emission from  $\text{H}_2\text{O}$  and  $\text{NO}_2$  at 6 to 7 micrometers has been assessed, and these effects can explain the apparent day/night differences in the  $\text{H}_2\text{O}$  retrieved from the LIMS radiances. A proposed  $\text{H}_2\text{O}$  reference model relies on the LIMS nighttime values, as a result. Heating from the reaction  $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$  is a major source of energy for the upper mesosphere. Until now, this reaction has been neglected in energy balance models of that region.

### Publications

Remsberg, E. E., K. V. Haggard, and J. M. Russell III, 1990: Estimation of Synoptic Fields of Middle Atmosphere Parameters from Nimbus 7 LIMS Profile Data. J. Atmos. and Oceanic Tech., 7, 689-705.

Miles, T. and W. L. Grose, 1989: Comparisons of Geostrophic and Non-Linear Balanced Winds from LIMS Data and Implications for Derived Dynamical quantities. PAGEOPH, 130, Nos. 2/3, 319-342.

Miles, T., and A. O'Neill, Eds., 1989: Comparison of Satellite-Derived Dynamical Quantities for the Stratosphere of the Southern Hemisphere. NASA Conf. Publ. 3044, 42 pp.

Fairlie, T. D. A., M. Fisher, and A. O'Neill, 1990: The Development of Narrow Baroclinic Zones and Other Small-Scale Structure in the Stratosphere During Simulated Major Warmings. Q. J. R. Meteorol. Soc., 116, 287-315.

Fairlie, T. D. A., A. O'Neill, and V. D. Pope, 1990: The Sudden Breakdown of an Unusually Strong Cyclone in the Stratosphere During Winter 1988/89. Q. J. R. Meteorol. Soc., 116, 767-774.

Kerridge, B. J. and E. E. Remsberg, 1989: Evidence from LIMS Data for Non-Local Thermodynamic Equilibrium in the  $\nu_2$  mode of Mesospheric Water Vapor and the  $\nu_3$  Mode of Stratospheric Nitrogen Dioxide. J. Geophys. Res., 94, 16323-16342.

Remsberg, E. E., J. M. Russell III, and C-Y. Wu, 1990: An Interim Reference Model for the Variability of the Middle Atmosphere Water Vapor Distribution. Adv. in Space Res., 10, No. 6, 51-64, (See also MAP Handbook 31)

Mlynczak, M. G. and S. Solomon, 1991: Middle Atmosphere Heating by Exothermic Chemical Reactions Involving Odd-Hydrogen Species. Geophys. Res. Letts., 18, 37-40.



The Reduction and Analysis of SME UV Data  
NAGW-1742

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ABSTRACT

The objective of this study is to use the long wavelength data near 310 nm from the ultraviolet spectrometer on SME to derive ozone density and mixing ratio profiles in the region from 3.0 to 1.0 mbar. The SME UVS data are unique in that they overlap with data from the NIMBUS-7 SBUV in the upper stratosphere in the 1983 - 1985 time period, and are coincident with SAGE II measurements beginning in late 1984. The SME measurements represent an opportunity for intercomparison of data in a region where ozone is believed to be most sensitive to changes in important minor constituent densities.

## SUMMARY OF PROGRESS

We have completed two years of the grant period. The instrument calibration and its time rate of change are needed for the inversion of the data. The calibration is used to refine the altitude determination by comparing the measured Rayleigh scattered signal to the results of a radiative transfer model. The relative change in the calibration has been determined and the final radiance data base has been generated.

The inversion technique used on the standard, shorter wavelength data has been modified for the longer wavelengths. The software has been tested. Individual inversions have been compared to ROCOZ and SAGE II data. Initial comparisons appear to give excellent agreement.

The remaining task is to invert the entire radiance data base for ozone and to compare the results to other instruments.

## Analysis of Stratospheric Aircraft Observations

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### Abstract

This investigation focuses on the interpretation and analysis of the AASE and AAOE aircraft measurements of radicals and conservative trace species. The interpretation is facilitated by the use of National Meteorological Center global meteorological analysis which is used to produce balanced winds and potential vorticity. A new method has been developed which allows the reconstruction of global maps of tracers from limited and isolated observations. This method along with trajectory model estimates of the mixing rates has allowed the computation of large scale tracer fluxes in the vortex region.

### Summary of Progress and Results

After the 1987 Airborne Antarctic Ozone Experiment (AAOE), it was realized that global meteorological analysis were not widely available to the aircraft experimenters. Yet, this global data was key to interpreting the constituent observations. For the 1989 Airborne Arctic Stratospheric Expedition (AASE) we proposed the development of meteorological data products tailored to the needs of the aircraft experimenters. These products included the projection of global meteorological data products onto the instrument field of view, and were made available to the experimenters on site. During AASE we also field tested the transmission of digital NMC forecast products and a new lee wave cloud forecast model. Our analysis products were widely used by AASE investigators. For example, the Langley DIAL lidar data could be processed quickly to convert ozone number density to mixing ratio with the aid of the NMC temperature analysis projected onto the lidar data.

For AASE II, which begins October 1991, we have developed a greatly expanded set of products to be made available to investigators in the field. In addition to the global meteorological analysis, these products include: 12 hr to 10 day forecasts of stratospheric fields, raw radiosonde data from near by sites, a user driven trajectory model, a high and low resolution lee wave model, a wide band radiative transfer model which includes the effects of PSC's, routine reconstruction of constituent data using the reconstruction method developed by Schoeberl and Lait, and routine computation of potential vorticity from flight data.

The development of these data products has been partly motivated by our desire to better understand the vortex structure and to shed light on the important question of vortex "leakiness" and the internal vortex mixing processes. In this regard, the trajectory model and radiative transfer model have been used to produce a coherent and comparative picture of the northern hemisphere (NH) and southern hemisphere (SH) polar vortex. The analysis shows that both vortices are highly isolated, and little mass transfer takes place across the vortex edge. A zone of adiabatic descent

surrounds each vortex with the resultant warming balanced by radiative cooling. Interior to the vortex there is little vertical motion, thus the larger size of the SH vortex more closely approaches radiative equilibrium temperatures since the center of that vortex is further removed from the heating at the jet core descent zone. This description of the vortex seems consistent with the observed tracer distributions which define a sharp edge crossing from mid-latitudes to the vortex interior. During AASE II we will be concentrating on the evolution of the tracer distribution in the fall and early winter.

#### Journal Publications (1990-1991)

1. "Airborne Lidar Observations in the Wintertime Arctic Stratosphere: Ozone," E. V. Browell, C. F. Butler, S. Ismail, M. A. Fenn, S. A. Kooi, A. F. Carter, A. F. Tuck, O. B. Toon, M. H. Proffitt, M. Loewenstein, M. R. Schoeberl, I. Isaksen, and G. Braathen, *Geophys. Res. Lett.*, **17**, 325-328, 1990.
2. "Stratospheric Temperatures During the 88-89 Northern Hemisphere Winter," P. A. Newman, L. R. Lait, M. R. Schoeberl, and R. M. Nagatani, *Geophys. Res. Lett.*, **17**, 329-332, 1990.
3. "Radiative Heating Rates During the Airborne Arctic Stratospheric Experiment," J. E. Rosenfield, M. R. Schoeberl, L. R. Lait, P. A. Newman, M. H. Proffitt, and K. K. Kelly, *Geophys. Res. Lett.*, **17**, 345-348, 1990.
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8. "Reconstruction of O<sub>3</sub> and N<sub>2</sub>O Fields from ER-2, DC-8, and Balloon Observations," L. R. Lait, M. R. Schoeberl, P. A. Newman, M. H. Proffitt, M. Loewenstein, J. R. Podolske, S. E. Strahan, K. R. Chan, B. Gary, J. J. Margitan, E. Browell, M. P. McCormick, and A. Torres, *Geophys. Res. Lett.*, **17**, 521-524, 1990.
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  14. "The Dynamics of the Polar Vortex," M. R. Schoeberl and D. L. Hartmann, *Science*, **251**, 46-52, 1991.
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  18. "The Structure of the Polar Vortex," M. R. Schoeberl, L. R. Lait, P. A. Newman, J. E. Rosenfield, *J. Geophys. Res.* (in press), 1991.
  19. "Stratospheric Temperatures During AASE: Results From STRATAN," R. B. Rood, P. A. Newman, D. J. Lamich, L. R. Lait, and R. Chan, *Geophys. Res. Lett.*, **17**, 337-340, 1990.
  20. "Three Dimensional Simulation of Hydrogen Chloride and Hydrogen Fluoride during the Airborne Arctic Stratospheric Expedition," J. A. Kaye, A. R. Douglass, R. B. Rood, R. S. Stolarski, P. A. Newman, D. J. Allen, E. M. Larson, M. T. Coffey, W. G. Mankin, and G. C. Toon, *Geophys. Res. Lett.*, **17**, 529-532, 1990.
  21. "Spatial and Temporal Variability of the Extent of Chemically Processed Stratospheric Air," J. A. Kaye, A. R. Douglass, R. B. Rood, R. S. Stolarski, P. A. Newman, D. J. Allen, and E. M. Larson, *Geophys. Res. Lett.*, **18**, 29-32, 1991.
  22. "Depletion of Arctic Ozone in the Winter 1990," M. Koike, Y. Kondo, M. Hayashi, Y. Iwasaka, P. A. Newman, M. Helten, P. Amedieu, *Geophys. Res. Lett.*, **18**, 791-794, 1991.

# Impact of Stratospheric Aerosols and Tropospheric Clouds on Stratospheric Photodissociation, Heating and Cooling Rates.

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**Research Objectives:** To develop an accurate and fast radiation model for the calculation of stratospheric photodissociation, heating and cooling rates. Particular emphasis is placed on the radiative coupling between the stratosphere and the troposphere due to scattering from clouds and aerosols. The model will be used to explore the impact of tropospheric clouds and stratospheric aerosols on stratospheric photolysis and heating/cooling rates.

## Summary of Progress and Results

To calculate photodissociation, heating and cooling rates, the radiation field in the atmosphere must be known. This radiation field is found by solving the radiative transfer equation pertinent to radiation transport in vertically inhomogeneous, absorbing, emitting and multiple scattering media. Based on previous work, we have extended our radiation algorithm to include a computationally efficient treatment of the vertical inhomogeneity (Kylling and Stamnes, 1991a) as well as spherical effects important for solar zenith angles greater than  $75^\circ$  (Dahlback and Stamnes, 1991). As computational speed is a concern in this kind of work, we have also developed a rapid two-stream radiative transfer solver (Kylling and Stamnes, 1991b).

We have used this fast radiation algorithm to develop a model which calculates photodissociation rates for a variety of molecular species pertinent to modelling of the chemistry of the stratosphere. We have applied the model to calculate photodissociation rates for a number of solar zenith angles (including zenith angles greater than  $90^\circ$ ) for a clear scattering and absorbing atmosphere. It has also been tested in a state-of-the-art 2-D stratospheric chemistry model provided to us by G. Brasseur at the National Center for Atmospheric Research.

We are presently incorporating a water cloud model into the scheme for calculating photodissociation rates. Later an aerosol model will be included. Work is underway to calculate heating and cooling rates.

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Research Task:

**ANALYSIS OF STRATOSPHERIC TRACE GAS SATELLITE MEASUREMENTS**

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**ABSTRACT OF RESEARCH OBJECTIVES:**

The stratospheric trace gas constituents methane ( $\text{CH}_4$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ) are important greenhouse gases and links in the chain leading to ozone depletion. Moreover, as long-lived tracers of stratospheric circulation, knowledge of their distribution and transport provides critical assessment of global stratospheric circulation models. The objectives of this new grant are to determine the three-dimensional and temporal variability of satellite-derived global measurements of methane and nitrous oxide from three years of Stratospheric And Mesospheric Sounder (SAMS) data fields, and to use these in dynamical calculations to determine the circulation in the stratosphere and lower mesosphere. The results will be compared with existing model calculations.

**SUMMARY OF PROGRESS AND RESULTS:**

1. Upper stratospheric photochemical lifetimes are estimated *in situ* for  $\text{CH}_4$  and  $\text{N}_2\text{O}$  for the first time, based on an analysis technique using 3 years of satellite measurements from the Stratospheric And Mesospheric Sounder (SAMS) instrument. The technique involves investigation of the time dependence of tracers injected into high Northern latitudes in late winter and their subsequent photochemical decay during the dynamically quiescent summer stratosphere. Dynamical corrections are made for mean meridional circulation contributions. The lifetimes for  $\text{N}_2\text{O}$  at 2 and 7 hPa ( $\sim 43$  and  $\sim 35$  km altitude) are found to be 1.7 and 8.3 months, respectively. For  $\text{CH}_4$ , 0.6 ( $\sim 52$  km altitude) and 2 hPa lifetimes are 3.3 and 3.4 months, respectively. These observed values are in good agreement with model calculations by Solomon et al. (1986). The lifetime estimates are used in dynamical calculations of the large-scale circulation.

2. Stratospheric circulation features are being investigated by further analyses of 3 years of SAMS data. Careful processing and analysis reveals pulse-like perturbations which are interpreted as zonal mean parcel motions.

(a) In the upper stratosphere and lower mesosphere, clear "pulses" are found which



exhibit a combination of seasonal upwelling and latitudinal propagation away from low latitudes towards both poles. The effect produces a strong semiannual component in both constituents and is stronger in the Southern Hemisphere (SH).

(b) The lack of a clear SH spring "double peak" in methane and nitrous oxide, compared with that observed in the NH spring, is attributed to enhanced tropical concentration in October caused by vertical transport from the semiannual component, combined with a stronger NH summer/autumn annual component.

(c) Circulation dynamics are investigated from two different perspectives:

(i) The effective transport formalism is used, together with a novel calculation technique, to derive both the zonal mean effective transport velocity ( $\bar{v}^{\dagger}, \bar{w}^{\dagger}$ ) field and eddy diffusion tensor  $K_{yy}$  distributions as a function of time, height and latitude in the meridional plane. The ( $\bar{v}^{\dagger}, \bar{w}^{\dagger}$ ) fields are consistent with models, including showing tropical vertical motion in October in contrast to the downward motion determined by an earlier study based on SAMS. Consistent with several earlier investigations, our  $K_{yy}(p, \phi, t)$  fields, determined in a self-consistent way, are strongly dependent on pressure, latitude, and time.

(ii) The Transformed Eulerian Mean formulation, together with calculated residual mean wind ( $\bar{v}^*, \bar{w}^*$ ), is also used to study stratospheric constituent distributions. Estimates of the residual term  $\nabla \cdot M$  in the transport equation delineate regions/times in which significant changes occur in constituent mixing ratio due to non-linear, transient, diabatic or non-conservative effects. Significant regions of non-zero  $\nabla \cdot M$  are found in the stratosphere in all seasons, not only in the NH winter high latitudes (where contributions from non-linear and non-steady perturbations in sudden and final warming events are expected), but also in the midlatitude, middle stratosphere in autumn and at winter-summer low latitudes near the stratopause. Some of these regions may be due to inadequate representation of the actual wind field by the residual mean wind estimates.

(d) Evidence is also found for significant NH autumnal vertical and poleward transport at high latitudes in the lower mesosphere.

#### JOURNAL PUBLICATIONS:

1. J. L. Stanford and J. R. Ziemke, 1991: CH<sub>4</sub> and N<sub>2</sub>O Photochemical Lifetimes in the Upper Stratosphere: *in situ* estimates using SAMS data. *Geophys. Res. Letts.*, 18, 677-680.
2. J. L. Stanford, J. R. Ziemke and S. Y. Gao, 1991: Stratospheric Circulation Features Deduced from SAMS Constituent Data. *J. Atmos. Sci.* (to be submitted for publication).

A. Analysis of Stratospheric Ozone, Temperature, and Minor Constituent Data

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C. Research Objectives

The objective of this research is to use available satellite data and model results to test the conceptual picture of stratospheric chemistry and transport. This can be broken down into two sub-goals: first, to use the data from TOMS and SBUV to observe the changes which are occurring in stratospheric ozone and second, to examine constituent transport processes emphasizing the possible role of heterogeneous reactions in causing the observed trends. The overall emphasis is on searching for constraints to theories.

D. Progress and Results

The most visible result of this research has been our analysis of the reprocessed TOMS total ozone data. We used a statistical model including trend, solar cycle, quasi-biennial oscillation, and noise terms to evaluate the nearly 12 year TOMS record. We found a trend in the data which was essentially zero at the equator and increased towards both poles. The southern hemisphere decrease appears to be consistent with dilution of the effects of the Antarctic ozone hole. The northern hemisphere midlatitude decrease was 0.4 to 0.5 %/year on an annual average or about 5% over the data record. This is significantly larger than the predictions of gas-phase photochemical models. The northern midlatitude decrease showed a strong seasonal variation with maximum in winter of greater than 0.8 %/year and minimum in summer of less than 0.2 %/year.

Our modelling work is focussed on attempts to explain these northern midlatitude ozone decreases. We have used the 2D photochemical model of Jackman and Douglass to evaluate the idea that the reaction of  $\text{N}_2\text{O}_5$  and  $\text{H}_2\text{O}$  on background sulfuric acid particles can modify the chlorine chemistry to significantly

enhance its effect on ozone. Our study shows that inclusion of this reaction leads to prediction of extremely small concentrations of  $\text{NO}_x$ . Since such small  $\text{NO}_x$  concentrations are not observed and  $\text{NO}_x$  is the key intermediary species which allows the reaction to perturb  $\text{ClO}$ , there are significant difficulties with this theory.

We have also used our 3D transport and chemistry model to examine the possibility that heterogeneous reactions on polar stratospheric clouds could provide the required modifications of chlorine chemistry and that these could then be transported from the vortex to low latitudes where the sunlight would initiate ozone destruction. This is a continuation of work originally started as part of the AASE mission. This study also demonstrates a difficulty with the theory. The 3D transport model, which is based on dynamical fields from a 4D data assimilation model, indicates far too little transport to low latitudes in the early winter to explain the satellite observations.

#### E. Journal Publications in 1990 and 1991

Kaye, J. A., A. R. Douglass, R. B. Rood, R. S. Stolarski, P. A. Newman, D. J. Allen, E. M. Larson, M. T. Coffey, W. G. Mankin, and G. C. Toon, "Three dimensional simulation of hydrogen chloride and hydrogen fluoride during the Airborne Arctic Stratospheric Expedition", *Geophys. Res. Lett.* 17, 529-532, 1990.

P. A. Newman, R. S. Stolarski, M. R. Schoeberl, L. R. Lait, and A. J. Krueger, "Total ozone during the 88-89 northern hemisphere winter", *Geophys. Res. Lett.*, 17, 317-320, 1990.

R. S. Stolarski, M. R. Schoeberl, P. A. Newman, R. D. McPeters, and A. J. Krueger, "The 1989 Antarctic ozone hole as observed by TOMS", *Geophys. Res. Lett.*, 17, 1267-1270, 1990.

A. R. Douglass, R. B. Rood, J. A. Kaye, and R. S. Stolarski, "The influence of polar heterogeneous processes on reactive chlorine at middle latitudes: three dimensional model implications", *Geophys. Res. Lett.*, 18, 25-28, 1991.

J. A. Kaye, A. R. Douglass, R. B. Rood, R. S. Stolarski, P. A. Newman, D. J. Allen, and E. M. Larson, "Spatial and temporal variability of the extent of chemically processed stratospheric air", *Geophys. Res. Lett.*, 18, 29-32, 1991.

P. A. Newman, R. S. Stolarski, M. R. Schoeberl, R. D. McPeters, and A. J. Krueger, "The 1990 Antarctic ozone hole as observed by TOMS", *Geophys. Res. Lett.*, 18, 661-664, 1991.

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A. Studies of Stratospheric Particulates (Task 579-22-04-10 )

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C. Research Objectives:

The principal objective of this work is to quantify the importance of heterogeneous chemistry to ozone depletion in the polar regions. The ambient stratospheric sulfate layer, and especially clouds in the polar stratosphere may provide surfaces upon which reactions occur and they may sequester or remove materials from the stratosphere. Our goals are to theoretically simulate such heterogeneous processes so that we may better quantify their importance, and so that we can identify processes that need to be studied in the laboratory. A sophisticated computer model of polar stratospheric clouds has been developed and used to study the properties of nitric acid clouds and ice clouds as well as their interactions with stratospheric gases. The model has been applied to interpret data collected during recent expeditions to the Antarctic and the Arctic.

D. Progress and Results:

A sophisticated numerical model of polar stratospheric cloud microphysics has been developed and used to simulate the mechanisms of denitrification of the polar stratospheres. It is found that denitrification can proceed by a variety of mechanisms. Falling nitric acid particles, formed in an environment which cooled slowly and remained cold for a week or more, can denitrify the air without removing water vapor. Falling ice crystals can remove both water vapor and nitric acid, but may require a considerable period of time to remove nitric acid (a week) due to the slow vapor phase transport in the presence of preexisting nitric acid particles. Hence, dehydration can occur with or without denitrification.

We also explored the radiative effects of polar stratospheric clouds. Except for optically thick pscs, such as in wave clouds, the cooling or heating rates of these clouds appear to be small. However, we find that the presence or absence of cirrus near the tropopause can significantly

impact the magnitude and sign of the heating rates in the polar stratosphere.

E. Journal Publications:

O. B. Toon, R. P. Turco, and P. Hamill Denitrification mechanisms in the polar stratospheres, *Geophys. Res. Lett.*, 17, 445-448, 1990. S. Kinne and O. B. Toon, Radiative effects of polar stratospheric clouds, *Geophys. Res. Lett.*, 17, 373-376, 1990.

**“Investigation of the Physics and Physical Chemistry of Polar Stratospheric  
Clouds, and Implications for the Ozone Hole”**

**Contract NASA/W-NAGW-2183**

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## Research Objectives

Investigate the chemical and physical processes related to stratospheric ozone change that involve polar stratospheric clouds (PSCs) and reactions occurring on the surfaces of PSC particles. Analyze the formation processes and properties of PSCs that are relevant to atmospheric chemistry and to the interpretation of field measurements taken during polar stratospheric missions. Study the physical and chemical behavior of ices that form in the stratosphere, including their interactions with gaseous species. Develop quantitative models of the microphysics of PSCs and the (heterogeneous) chemical processes occurring on ice surfaces. Carry out simulations of denitrification and dehydration by PSCs to determine the dominant mechanisms. Assimilate laboratory and field data into these models, and apply them to make estimates of the extent of chemical processing on PSCs and the impact of specific microphysical processes on polar composition and polar ozone depletion. Couple the microphysics and heterogeneous chemistry processes to a dynamical model of the polar stratospheric circulation to investigate the nature of the interactions between dynamics and heterogeneous chemistry.

## Summary of Progress and Results, 1990/91

During the first year of this project, three specific research areas received attention: polar stratospheric cloud microphysics and physical chemistry; models of heterogeneous chemistry on PSCs; and nucleation phenomena in the stratosphere.

Microphysics and Physical Chemistry: We have completed studies on the physical chemistry of polar stratospheric clouds (PSCs), deducing that the maximum concentrations of HCl in stratospheric ice crystals will be only  $\sim 10^{-6}$  molar (Elliott et al., 1990, 1991). Fast heterogeneous chemical reactions involving HCl require condensation of HCl onto the ice surface or onto defect sites near the ice surface. A detailed PSC microphysics model was also developed, which can simulate the formation, evolution and composition of polar stratospheric clouds, and the overall rates of heterogeneous reactions occurring on the cloud particles. The model was used to study the dehydration and denitrification mechanisms of the polar stratosphere (Toon et al., 1990; Drdla and Turco, 1991), showing how both Type-I and Type-II particles participate in denitrification. Moreover, temperature oscillations associated with synoptic-scale motions were shown to control the properties of the PSCs and the mode of denitrification. The model has been applied to estimate the degree of chemical processing that can occur on PSCs through ice catalyzed reactions (Drdla et al., 1991a). It is found that chlorine activation occurs almost exclusively on Type-I particles early in the winter, and that the principal chlorine byproduct is chlorylnitrate. We have prepared to participate in NASA's Arctic Ozone mission this winter; a trajectory model incorporating PSC microphysics and heterogeneous chemistry, as described above, will be used in the field to interpret

aircraft data and to predict PSC and chemical states along proposed flight tracks. Another collaboration has been established with the laboratory group of M.-T. Leu at JPL (Moore et al., 1990), to interpret measurements of heterogeneous reaction rates. We have also acted to review and disseminate scientific data from NASA's stratosphere programs (e.g., Turco, 1990a,b; Turco et al., 1990; Toon and Turco, 1991).

**Models of Heterogeneous Chemistry:** A unique model has been developed that describes the basic surface physics and chemistry processes on ice particles (Tabazadeh and Turco, 1991). The model predicts the mass transfer rates between the gas and aerosol phases, and determines the rate-limiting physical and chemical factors. In the past, ozone hole chemistry models had simply fixed the rates of heterogeneous reactions using "sticking coefficients" measured in the laboratory. Our surface physics model is being integrated into the PSC microphysics model described above (Drdla et al., 1991a). The combined surface chemistry/microphysics model is also being integrated with a gas-phase photochemistry module developed at UCLA. This detailed microphysics-chemistry model can then be driven by a three-dimensional trajectory model developed by C. R. Mechoso and co-workers at UCLA, allowing fully-interactive simulations of polar dynamics, microphysics and chemistry to be carried out. The model is being applied to study the key processes controlling chlorine activation and denitrification on PSCs (Drdla et al., 1991b), and to guide other theoretical and experimental research.

The potential for chlorine activation through chemical reactions on sulfate aerosols has been evaluated for special circumstances that occur in the stratosphere (Turco and Hamill, 1991). Time constants have been calculated for chlorine activation and de-NO<sub>x</sub>-ification on the highly-water-diluted sulfate aerosols that are found at temperatures below about 205 K (but above the frost point for PSC Type-I formation). The chemical activity of the sulfate aerosol is greatly enhanced under such conditions, and most of the chlorine reservoirs might be activated by this mechanism; hence, substantial ozone depletions may be possible in air that never encounters PSCs.

**Nucleation Phenomena:** A new, highly-efficient algorithm has been developed for calculating the nucleation rates of ice crystals and sulfuric aerosols in the stratosphere and in volcanic eruption plumes (Zhao and Turco, 1991). Both homogeneous and heterogeneous nucleation rates are treated. The observed sudden appearance of sulfuric acid aerosols in the polar stratosphere in spring can be explained with the model (Hamill et al., 1990; Zhao et al., 1991). The rapid particle formation is associated with high sulfuric acid vapor concentrations produced between 25 and 30 km when carbonyl sulfide is photodissociated at polar sunrise.



### **Publications Supported Under This Grant**

- Drdla, K., and R. P. Turco, "Denitrification through PSC formation: A 1-D model incorporating temperature oscillations", J. Atmos. Chem., **12**, 319-366 (1991).
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- Zhao, J., O. B. Toon and R. P. Turco, "Homogeneous nucleation of sulfate aerosols in the polar springtime stratosphere", Abstract, EOS, American Geophysical Union, in press (1991).

- A. **TITLE OF RESEARCH TASK:** A Study of the Variations of Nitrogen Dioxide Using SME and SAGE Data
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- Dr. Ronald J. Thomas  
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- C. **ABSTRACT:** A proposal to investigate the behavior of stratospheric NO<sub>2</sub> during the period from 1979 through 1990. The NO<sub>2</sub> measurements from the Stratospheric Aerosol and Gas Experiment (SAGE I) (1979-1981), the Solar Mesosphere Explorer (SME) (1982-1986), and SAGE II (late 1984-present) will be incorporated into a single unified data base. Because of the diurnal variability of NO<sub>2</sub>, the SME late afternoon measurements will have to be converted to local sunset using an improved photochemical model. A detailed intercomparison during the period of overlap between SME and SAGE II will allow for the assessment of any systematic differences between the individual data sets. Once assembled, the unified data base will be used to investigate the daily, seasonal, interannual, and long-term variability of NO<sub>2</sub> in the region from 24 to 38 km.
- D. **RESULTS TO DATE:** A unified data base built from data sets which have fundamentally different spatial and temporal sampling has to be placed on a common grid. Realizing that the SAGE I and SME data sets are static and that the continuing measurements from SAGE II have essentially the same sampling as SAGE I, it was decided that the SME measurements would be converted from their local time of between 3 and 6 p.m. to the sunset local time of the SAGE measurements. It was also decided that the data would be placed onto a pressure grid and NO<sub>2</sub> values converted to mixing ratios.

The photochemical model for the partitioning of odd nitrogen compounds, which is required to convert NO<sub>2</sub> to different local times, has been extensively upgraded. This model requires several input parameters, ozone and temperature in

particular. The ozone used in the model is based on MAP climatology for long-term studies, or the SAGE II climatology for studies of short-term variability. The temperature data is obtained from the NMC analysis. Since the diurnal variation of NO<sub>2</sub> is dominated by the photolysis of NO<sub>2</sub>, the local time conversion process is especially sensitive to changes in the photolysis rates.

The model has also been substantially improved by upgrading the radiative transfer calculation for the photolysis rates. This calculation now uses spherical geometry for the direct solar flux and then includes a two stream model for multiple scattering. Again as in the chemical model, the important absorbing species such as ozone are taken from well established climatologies. These new photolysis rates are now a function of day of year, altitude, latitude, and solar zenith angle.

The SME data set has been converted to local sunset. An intercomparison between SME and SAGE during 1984-1986 has shown that there are systematic differences between the two data sets, but these are within their known uncertainties. Since the SAGE II NO<sub>2</sub> data set is probably the best validated of the data sets, the SME data is adjusted, within its error limits, to agree with the SAGE II data. When adjusted, all three sets of data exhibit the same seasonal behavior. This seasonal behavior has recently been presented at two conferences and is the subject of an upcoming publication.

A major result obtained so far has been the discovery of the Quasi-Biennial Oscillation (QBO) of NO<sub>2</sub>. The QBO has long been observed in the equatorial wind, ozone, and temperature fields. More recently, models have been investigating the QBO in other trace species. Based primarily on the six years of SAGE II data, the first observational evidence for a QBO in NO<sub>2</sub> has been obtained and quantified.

Investigations of longer term variability requires a well calibrated data set of uniform quality. To this end, a cooperative effort between these researchers and the DSIR group in New Zealand has begun. The DSIR group has made nearly continuous ground-based measurements of the NO<sub>2</sub> column abundance since 1979. Intercomparisons with their data should reveal long-term changes in the quality of the satellite data sets.

E. JOURNAL PUBLICATIONS:

Zawodny, J. M., and M. P. McCormick: Stratospheric Aerosol and Gas Experiment II Measurements of the Quasi-Biennial Oscillations in Ozone and Nitrogen Dioxide, Journal of Geophysical Research, **96**, 9371-9377, 1991.



C. GLOBAL CHEMICAL MODELING

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## RESEARCH SUMMARY

A. Modeling of Chemistry and Transport in a Multi-Dimensional Model of the Terrestrial Middle Atmosphere (NAGW-413)

B. Yuk L. Yung, California Institute of Technology, Principal Investigator; Mark Allen, Richard W. Zurek and David Crisp, Jet Propulsion Laboratory, Co-Investigators.

C. Abstract: The focus of our research program is the achievement of a quantitative understanding of the spatial distribution and temporal variation of chemical species in the terrestrial middle atmosphere, with emphasis on ozone. Our activities contribute to a refinement of model descriptions of chemical and dynamical processes that are needed for assessment tasks. A unique feature of our research effort is a close interaction with the chemical kinetics group at JPL and the field measurement groups at JPL. The principal tools used in our investigations are 1-D and 2-D photochemical models. The advective component of the meridional transport in these models is approximated by the diabatic circulation, which is derived diagnostically from the net radiative heating rates. We are developing accurate radiative transfer algorithms to find the net heating rates and the diabatic circulation for use in the 2-D model.

D. Current Work: Highlights of recent results include (1) use of a novel mapping technique for studying TOMS  $O_3$  data, together with our 1-D photochemical model, to quantitatively estimate  $O_3$  loss rates in the springtime Antarctic stratosphere; (2) study of the impact of the El Chichon eruption upon the chlorine budget of the low latitude stratosphere; this work is also applicable to the recent Mt. Pinatubo eruptions; (3) tests of current photochemical models using Spacelab 3 ATMOS observations; and (4) development of a new class of radiative transfer technique called spectral mapping transformations. These highlights will be amplified below.

### **Spatial Variation of Ozone Depletion Rates in the Springtime Antarctic Polar Vortex**

An area-mapping technique was applied to the Nimbus 7 TOMS (Total Ozone Mapping Spectrometer) data to filter out synoptic perturbations of the Antarctic polar vortex such as distortion or displacement away from the pole, revealing the detailed morphology of the temporal chemical evolution of column  $O_3$ . The results for the austral spring of 1987 suggest the existence of a relatively stable collar region enclosing an interior undergoing large variations. There is tentative evidence for quasiperiodic (15-20 days)  $O_3$  fluctuations in the collar, and for upwelling of tropospheric air in late spring. With a simplified photochemical model, the evolution with time of the area-mapped polar ozone constrains the chlorine monoxide (ClO) concentrations in the springtime Antarctic vortex.

### **Heterogeneous Reactions with NaCl in the El Chichon Volcanic Aerosols**

Previous investigations of the effects of the 1982 eruption of the El Chichon volcano could not explain all the observations of changes in  $O_3$ , HCl, NO, and  $NO_2$  simultaneously without proposing speculative chemical reactions. Since reactions between solid NaCl and gaseous  $NO_2$ ,  $ClNO_3$  and  $N_2O_5$  do produce photochemically active chlorine species and solid  $NaNO_3$  in laboratory experiments, we suggest that these reactions could have occurred with the NaCl observed to be present in the El Chichon sulfuric acid aerosols. As a consequence, we predict that HCl should increase substantially, while  $NO_x$  should decrease, in agreement with the

measurements after the eruption.

### **Mapping transformations for broadband atmospheric radiation calculations.**

The principal objective of this work is to develop improved numerical radiative transfer models for finding solar heating rates, thermal cooling rates, and the diabatic circulation at these levels of the atmosphere. The current radiative transfer model is undergoing major modifications to increase its speed, accuracy, and versatility. The original Voigt quasi-random model is being replaced by a new class of methods called spectral mapping transformations (SMT's), that were developed as part of this program. Preliminary tests of this new method have demonstrated accuracies comparable to those of line-by-line models, and speeds like those obtained with simpler band models. Results from the new radiative transfer model will be incorporated into the Caltech/JPL 2d-chemical tracer transport model for simulations of the stratospheric hydrological cycle.

### **Test of Odd-Oxygen Photochemistry Using Spacelab 3 ATMOS Observations**

The ozone profile calculated using a one-dimensional time-dependent photochemical model, with recommended photocross-sections and reaction rate constants, is systematically less than the Spacelab 3 (May, 1985) ATMOS observations at sunset ( $\chi = 90^\circ$ ),  $30^\circ\text{N}$  latitude, throughout the upper stratosphere and mesosphere. Model results are  $\sim 9\%$  smaller than the nominal ATMOS  $\text{O}_3$  value at 40 km and 50% less at 76 km. Given the uncertainties associated with the ATMOS profile, the model "deficit" may be as large as 15% at 36 km, increasing to  $\sim 70\%$  at 76 km. A similar model  $\text{O}_3$  "deficit" exists at sunrise,  $47^\circ\text{S}$  latitude, in the stratosphere: nominal differences of  $\leq 25\%$ , increasing to  $\leq 45\%$  when the ATMOS uncertainties are considered. Model results closely approximate ATMOS observations in both the upper stratosphere and mesosphere upon enhancing odd-oxygen production by increasing the  $\text{O}_2$  Schumann-Runge and Herzberg cross-sections values used in the calculations.

### **E. Publications:**

- Allen, M., and Delitsky, M.L. 1990, Stratospheric  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}_5$ : A comparison of model Results with Spacelab 3 ATMOS measurements, *J. Geophys. Res.*, **95**, 14077-14082.
- Howell, C.D., Michelangeli, D.V., Allen, M., Yung Y.L. and Thomas, R.J. 1990, SME observations of  $\text{O}_2(^1\Delta)$  nightglow: An assessment of the chemical production mechanisms, *Planet. Space Sci.* **38**, 529-539.
- Shia, R.-L., Ha, Y.L., Wen, J.-S., and Yung, Y.L. 1990, Two-dimensional atmospheric transport and chemistry model: Numerical experiments with a new advection algorithm, *J. Geophys. Res.*, **95**, 7467-7483.
- West R.A., Crisp, D. and Chen, L. 1990, Mapping transformations for broadband atmospheric radiation calculations. *J. Quant. Spectrosc. Radiat. Transfer*, **43**, 191-199.
- Yung, Y.L., Allen, M., Crisp, D., Zurek, R.W. and Sander, S.P. 1990, Spatial variation of ozone depletion rates in the springtime Antarctic vortex, *Science*, **248**, 721-724.
- Allen, M., and Delitsky, M.L. 1991, Inferring the abundances of  $\text{ClO}$  and  $\text{HO}_2$  from Spacelab 3 ATMOS observations. *J. Geophys. Res.*, **96**, 2913-2919.
- Michelangeli, D.V., Allen, M., and Yung, Y.L. 1991, Heterogeneous reactions with  $\text{NaCl}$  in the El Chichon volcanic aerosols, *Geophys. Res. Lett.* **18**, 673-676.
- Allen, M., and Delitsky, M.L. 1991, A test of odd-oxygen photochemistry using Spacelab 3 ATMOS observations. *J. Geophys. Res.* in press.



## **Biennial Research Summary**

### **A. Project Title**

Two-Dimensional Modeling Studies of the Middle Atmosphere

### **B. Investigators**

Rolando R. Garcia, National Center for Atmospheric Research, Boulder, CO

Susan Solomon, NOAA/Aeronomy Laboratory, Boulder, CO

### **C. Research Objectives**

To investigate various processes that control transport of chemical species in the middle atmosphere. The investigation is to be carried out using a new numerical model which extends from the troposphere to the lower thermosphere and includes parameterizations for both gravity and planetary wave breaking. Topics to be examined include the roles of planetary and gravity wave driving in establishing observed distributions of chemical species, tropical circulations and their effects on quasi-biennial and semi-annual variability, and the influence of transport on the ozone depletion potential of halocarbons proposed as replacements for CFCs.

### **D. Progress and Results**

The model has been reformulated to include most of the troposphere above the boundary layer; the planetary wave breaking parameterization developed by Garcia (see below) has been incorporated; work is now underway to add the full complement of chemical reactions from the previous version of the Garcia-Solomon model. The previous version of the model was used to conduct studies of the formation of noctilucent clouds in the mesosphere, and of the response of the stratosphere to the 1989 solar proton event. The model has also been used to perform calculations of ozone depletion perturbation scenarios (WMO, 1990).

### **E. Publications**

Garcia, R.R., 1990: Dynamics, radiation and photochemistry in the mesosphere: Implications for the formation of noctilucent clouds. *J. Geophys. Res.*, *94*, 14605-14615.

Reid, G.C., S. Solomon and R.R. Garcia, 1991: Response of the middle atmosphere to the solar proton events of August-December, 1989. *Geophys. Res. Lett.*, *18*, 1019-1022.

Garcia, R.R., 1991: Parameterization of planetary wave breaking in the middle atmosphere. *J. Atmos. Sci.*, *48*, 1406-1419.

## BIENNIAL RESEARCH SUMMARY

### A. Grant Title

Stony Brook/GSFC Collaborative Studies in Stratospheric Studies with Chemistry Modelling

### B. Principal Investigator

Marvin A. Geller  
Institute for Terrestrial and Planetary Atmospheres  
State University of New York at Stony Brook  
Stony Brook, New York 11794-3800

### C. Research Objectives

The objective of this research was to continue the research collaboration between Marvin A. Geller at SUNY/Stony Brook and the SGCCM research group at the NASA Goddard Space Flight Center. Areas of potential collaboration were identified to be complementary data analysis studies, interpretative work on model results generated at NASA GSFC, and complementary mechanistic modeling studies.

### D. Summary of Progress and Results

Research progress on this task came in three principal areas, each of which can be identified by either a paper that has appeared in the journal literature, a paper that has been accepted for publication, or one that has has been submitted.

The first area is the improvement of our understanding of how the information content of mapped satellite observations relate to actual atmospheric behavior. Murray Salby published a series of papers on this topic during the 1980's that formally derived the temporal and spatial time scales that can be resolved by satellite sampling and subsequent mapping. We have taken a more concrete approach to this subject by flying a mathematical "satellite" through model results that were generated by the SGCCM group at NASA GSFC. The first results from this appeared in Rood et al. (1991). At least two other papers on this topic are in preparation.

A second area of research is a continuation of analysis of the stratospheric general circulation using the multi-year temperature

data set from NOAA/NMC extending from the Earth's surface to about 55 km. The paper by Geller et al. (1991) presents and interprets the results from calculations of monthly mean residual circulations for a period of eight years. The results of this paper pertain to interpretation of which areas of the stratosphere are under radiative control and which are under dynamic control as well as how transport processes control the interannual variability of ozone.

The third area of research is the connection between the stratospheric quasi-biennial oscillation (QBO) and sea surface temperatures. A QBO is known to exist in both the ocean and the tropical atmosphere. Zhang and Geller (1991) have examined a mechanism by which sea surface temperature variations can affect the equatorial waves that force the stratospheric QBO. They have also modeled how a QBO in the equatorial wave flux might affect the stratospheric QBO

#### E. Journal Publications

1. "Three-Dimensional Simulations of Wintertime Ozone Variability in the Lower Stratosphere," R. B. Rood, A. R. Douglass, J. A. Kaye, M. A. Geller, Y. Chi, D. J. Allen, E. M. Larsen, E. R. Nash, and J. E. Nielsen, J. Geophys. Res., 96, 5055-5071 , 1991.
2. "Residual Circulations Calculated from Satellite Data: Their Relations to Observed Temperature and Ozone Distributions," M. A. Geller, E. R. Nash, M. F. Wu, and J. E. Rosenfield, accepted for publication in J. Atmos. Sci., 1991.
3. "Selective Excitation of Tropical Atmospheric Waves and SST Modulation of the Stratospheric QBO. Submitted for publication in J. Atmos. Sci., 1991.

Title: GCM - Chemistry and Transport in the Stratosphere

Investigators and Institutions:

Principal Investigator: William L. Grose, Mail Stop 401B, NASA Langley Research Center, Hampton, Virginia 23665-5225

Co-Investigators: Ellis E. Remsberg, Richard S. Eckman, W. Thomas Blackshear, Richard E. Turner, R. Bradley Pierce, and David E. Siskind

All at NASA Langley Research Center

Collaborators: T. Duncan Fairlie, Science & Technology Corporation, 101 Research Drive, Hampton, Virginia 23666

Abstract of Research and Objectives

The overall objective is to achieve a more complete understanding of the role of atmospheric processes related to global change. Observational and modeling studies of radiative, chemical, and dynamical processes and their mutual interactions will be conducted. Observational studies will be undertaken utilizing meteorological and constituent data from ground-based, aircraft, balloon-borne, and satellite-borne experiments. Modeling studies will be conducted with a hierarchy of atmospheric simulation models.

Summary of Progress and Results

Scientific investigations for this period have concentrated on: (1) polar ozone depletion and dilution effects; (2) the annual cycle evolution of odd-nitrogen constituents in the stratosphere; and (3) dynamical and radiative processes in the stratosphere with emphasis on inter-hemispheric differences.

Simulations of the formation and evolution of the Antarctic ozone hole were conducted with a 3-D chemistry/transport model incorporating heterogeneous chemical processes. Comparisons of the results were made with TOMS ozone data, MSU and SSU meteorological data, conventional meteorological analyses, and the AAOE aircraft constituent data. The simulation results showed good agreement in most respects with the observations. The major deficiencies were a result of the relatively coarse model resolution. One year after formation of the ozone hole, a residual deficit in hemispheric ozone occurred as a result of dilution.

A 1-year simulation of the annual cycle evolution of odd-nitrogen constituents has been conducted with a 3-D chemistry/transport model. Extensive comparisons have been made with SAGE II, LIMS, ATMOS, SME, and balloon observations. The results showed excellent agreement with the observations in most respects. The major discrepancies were in chlorine nitrate and nitric acid. Total odd-nitrogen showed good agreement with ATMOS profile data. Ten years of SSU data have been analyzed to study stratospheric differences in dynamics. Comparisons between several classes of warming events (Canadian, minor, major, final) have been completed to study the differences and/or

commonality in the evolution in both hemispheres. Analysis of the SSU-inferred height distributions suggests the existence of preferential states in the stratosphere as indicated by a bimodal frequency distribution for wave number one amplitudes.

A number of model modifications and enhancements have also been accomplished this period. The LaRC 3-D atmospheric simulation model has been extended to the mesosphere, and a radiative transfer code incorporating non-LTE effects has been added. A higher resolution model (T42, 24 vertical levels) has been implemented. Heterogeneous chemical processes have been incorporated in the 3-D chemistry/transport model. The UKMO 3-D Mechanistic Stratosphere Mesosphere Model has been adapted to the LaRC computers, and a chemistry module developed for incorporation.

### Publications

Grose, W. L., R. S. Eckman, R. E. Turner, and W. T. Blackshear, 1990: Potential Effects of Antarctic Ozone Depletion on the Global Ozone Budget. Dynamics, Transport and Photochemistry of the Southern Hemisphere Middle Atmosphere. A. O'Neill (Ed.). Kluwer Academic Publ., Dordrecht, Netherlands.

Eckman, R. S., R. E. Turner, W. T. Blackshear, T. D. A. Fairlie, and W. L. Grose, 1991: Some Aspects of the Interaction Between Chemical and Dynamical Processes Relating to the Antarctic Ozone Hole. Adv. Space Res., Pergamon Press, Oxford, England.

Fairlie, T. D. A., A. O'Neill, and V. D. Pope, 1990: The Sudden Breakdown of an Unusually Strong Cyclone in the Stratosphere During Winter 1988/89. Q.J.R.M.S., 116.

Title: Observational and Modeling Studies of Radiative, Chemical, and Dynamical Interactions in the Earth's Atmosphere - EOS Data Information System

Investigators and Institutions:

Principal Investigator: William L. Grose, Mail Stop 401B, NASA Langley Research Center, Hampton, Virginia 23665-5225

Co-Investigators: Susan Solomon, NOAA Aeronomy Laboratory, Boulder, Colorado

A. O'Neill, United Kingdom Meteorological Office, Bracknell, England

M. Salby, University of Colorado, Boulder, Colorado

R. Garcia, National Center for Atmospheric Research Boulder, Colorado

W. Thomas Blackshear, Richard E. Turner, Ellis E. Remsberg, and Richard S. Eckman

All at NASA Langley Research Center

Abstract of Research and Objectives

The objectives are: (1) definition and implementation of an EOS Data Information System; (2) adaptation of existing model and data analysis codes to a UNIX environment; and (3) development of science analysis software for UARS data as an EOS precursor.

Summary of Progress and Results

An EOS Data Information System has been defined, and initial implementation of the system has taken place. A UNIX based system of five linked workstations has been acquired and operationally demonstrated. Significant storage capability in the form of hard disks has been linked to the workstations. Future storage expansion in the form of optical disk memory has been established with the LaRC mainframe computers, the UARS Remote Access Computer, and mainframe computers at Co-Investigator sites at NCAR and the UKMO.

A number of the hierarchy of models to be used in the associated EOS science investigation have been modified to a UNIX environment and implemented for operation on the workstations. Similar modifications have been conducted for existing data analysis software.

A substantial amount of science analysis software has been developed for UARS data. These software codes are for analysis of wind, temperature, and constituent data, as well as for derived quantities.

Publications

None

Title: Observational and Modeling Studies of Radiative, Chemical, and Dynamical Interactions in the Earth's Atmosphere - EOS Science

Investigators and Institutions:

Principal Investigator: William L. Grose, Mail Stop 401B, NASA Langley Research Center, Hampton, Virginia 23665-5225

Co-Investigators: Susan Solomon, NOAA Aeronomy Laboratory, Boulder, Colorado

A. O'Neill, United Kingdom Meteorological Office, Bracknell, England

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R. Garcia, National Center for Atmospheric Research Boulder, Colorado

W. Thomas Blackshear, Richard E. Turner, Ellis E. Remsberg, and Richard S. Eckman

All at NASA Langley Research Center

Abstract of Research and Objectives

The overall objective is to achieve a more complete understanding of the role of atmospheric processes related to global change. Observational and modeling studies of radiative, chemical, and dynamical processes and their mutual interactions will be conducted. Observational studies will be undertaken utilizing meteorological and constituent data from ground-based, aircraft, balloon-borne, and satellite-borne experiments. Modeling studies will be conducted with a hierarchy of atmospheric simulation models.

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Simulations of the formation and evolution of the Antarctic ozone hole were conducted with a 3-D chemistry/transport model incorporating heterogeneous chemical processes. Comparisons of the results were made with TOMS ozone data, MSU and SSU meteorological data, conventional meteorological analyses, and the AAOE aircraft constituent data. The simulation results showed good agreement in most respects with the observations. The major deficiencies were a result of the relatively coarse model resolution. One year after formation of the ozone hole, a residual deficit in hemispheric ozone occurred as a result of dilution.

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in most respects. The major discrepancies were in chlorine nitrate and nitric acid. Total odd-nitrogen showed good agreement with ATMOS profile data. Ten years of SSU data have been analyzed to study stratospheric differences in dynamics. Comparisons between several classes of warming events (Canadian, minor, major, final) have been completed to study the differences and/or commonality in the evolution in both hemispheres. Analysis of the SSU-inferred height distributions suggests the existence of preferential states in the stratosphere as indicated by a bimodal frequency distribution for wave number one amplitudes.

A number of model modifications and enhancements have also been accomplished this period. The LaRC 3-D atmospheric simulation model has been extended to the mesosphere, and a radiative transfer code incorporating non-LTE effects has been added. A higher resolution model (T42, 24 vertical levels) has been implemented. Heterogeneous chemical processes have been incorporated in the 3-D chemistry/transport model. The UKMO 3-D Mechanistic Stratosphere Mesosphere Model has been adapted to the LaRC computers, and a chemistry module developed for incorporation.

#### Publications

Grose, W. L., R. S. Eckman, R. E. Turner, and W. T. Blackshear, 1990: Potential Effects of Antarctic Ozone Depletion on the Global Ozone Budget. Dynamics, Transport and Photochemistry of the Southern Hemisphere Middle Atmosphere. A. O'Neill (Ed.). Kluwer Academic Publ., Dordrecht, Netherlands.

Eckman, R. S., R. E. Turner, W. T. Blackshear, T. D. A. Fairlie, and W. L. Grose, 1991: Some Aspects of the Interaction Between Chemical and Dynamical Processes Relating to the Antarctic Ozone Hole. Adv. Space Res., Pergamon Press, Oxford, England.

Fairlie, T. D. A., A. O'Neill, and V. D. Pope, 1990: The Sudden Breakdown of an Unusually Strong Cyclone in the Stratosphere During Winter 1988/89. Q.J.R.M.S., 116.



#### A. Fast Two-dimensional Model

#### B. Principal Investigator:

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#### Co-Investigators:

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#### C. Research Objectives

The objective of this research is to use a two-dimensional (altitude and latitude) model of the atmosphere to investigate problems relating to the variability of the dynamics and temperature of the atmosphere on the ozone distribution, variations of atmospheric constituents related to solar cycle changes, the sensitivity of model results to tropospheric trace gas sources, and assessment computations of changes in ozone related to manmade influences.

#### D. Progress and Results

The fast 2-D model allows us to investigate atmospheric effects and influences that are on short and long time-scales (days to a century) relatively easily. The model has been extended to 90 km in the past two years to include the mesosphere in order to allow a more realistic representation of upper atmosphere. The model has also been moved to our new IRIS workstation and requires about 30 minutes of computer time to simulate a model year.

The fast 2-D model has been used to investigate the effect of solar proton events on the middle atmosphere during the past two solar cycles. The odd nitrogen created by the August 1972 solar proton event was enough to cause an ozone depletion lasting several months. The model results of this ozone depletion compared reasonably well with the observations by the Nimbus IV Backscattered Ultraviolet instrument in the middle stratosphere.

We have investigated the interannual changes in ozone due to dynamical and temperature influences over the time period 1979-86 and have compared to Nimbus VII SBUV and TOMS measurements when possible. The observed interannual changes in ozone in the upper stratosphere are simulated with the 2-D model, however, observed interannual changes in total ozone are not well represented by the 2-D model. We suspect that a better 2-D formulation of the troposphere and its influence on the stratosphere is needed for a more realistic model simulation of the interannual behavior of total ozone.

We have used the 2-D model to investigate the effects of the Space Shuttle and Titan rockets on the chlorine budget of the stratosphere and its subsequent influence on ozone. The chlorine enhancements are small, on average less than 0.6% above the current background. The corresponding ozone decreases are at most 0.14%. The results of this study have been published in the Congressional Report in 1990 (NASA Reference Publication 1242).

We have investigated the abundance of three isotopes of methane,  $^{12}\text{CH}_4$ ,  $^{12}\text{CD}_4$ , and  $^{13}\text{CHD}_3$  with the 2-D model. Both  $^{12}\text{CD}_4$  and  $^{13}\text{CHD}_3$  are enhanced relative to  $^{12}\text{CH}_4$  because of their slower rates of loss by reaction with OH. Our model results have been compared with measurements which show enhancements a factor of 100 larger than we compute. We suggest that other natural or anthropogenic sources of  $^{12}\text{CD}_4$  and  $^{13}\text{CHD}_3$ , which are not known at present, need to be included in our future model computations.

A simulation of the key fluorine reservoir species was carried out and compared to measurements over the time period 1977-90. The model is in good qualitative agreement with observed vertical profiles of HF and  $\text{CF}_2\text{O}$ , but tends to underestimate the total column of HF.

The impact of the national aerospace plane on stratospheric chemistry and ozone was assessed. Effluents of  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , NO,  $\text{NO}_2$ , OH, H, and O from test flights of this plane will slightly perturb the stratosphere. Locally, ozone decreases by a maximum of 0.006% resulting mainly from the  $\text{HO}_x$  increases.

The effects of tropospheric trace gases on assessment scenario calculations was computed. Relatively large changes in tropospheric CO and  $\text{NO}_x$  result in modest changes in stratospheric  $\text{CHClF}_2$  through modifications in tropospheric OH abundance. For example, a doubling of tropospheric CO results in about a 10% increase in stratospheric  $\text{CHClF}_2$ .

We are involved in the 1991 United Nations Environmental Program (UNEP) assessment of the stratosphere. We have used our model in several scenarios of atmospheric conditions and have model predictions of ozone and other constituent changes through the year 2050 which will be used in the UNEP assessment.

#### E. Journal Publications

- Jackman, C. H., A. R. Douglass, R. B. Rood, R. D. McPeters, and P. E. Meade, Effect of solar proton events on the middle atmosphere during the past two solar cycles as computed using a two-dimensional model, J. Geophys. Res., 95, 7417-7428, 1990.
- Kaye, J. A., and C. H. Jackman, Comment on "Detection of multiply deuterated methane in the atmosphere," Geophys. Res. Lett., 17, 659-660, 1990.
- Prather, M. J., M. M. Garcia, A. R. Douglass, C. H. Jackman, M. K. W. Ko, and N. D. Sze, The Space Shuttle's impact on the stratosphere, J. Geophys. Res., 95, 18,583-18,590, 1990.
- Jackman, C. H., A. R. Douglass, S. Chandra, R. S. Stolarski, J. E. Rosenfield, J. A. Kaye, and E. R. Nash, Impact of interannual variability (1979-1986) of transport and temperature on ozone as computed using a two-dimensional photochemical model, J. Geophys. Res., 96, 5073-5079, 1991.
- Kaye, J. A., A. R. Douglass, C. H. Jackman, R. S. Stolarski, R. Zander, and G. Roland, Two-dimensional model calculation of fluorine-containing reservoir species in the stratosphere, J. Geophys. Res., 96, 12,865-12,881, 1991.
- Jackman, C. H., Effects of energetic particles on minor constituents of the middle atmosphere, Journal of Geomagnetism and Geoelectricity, in press, 1991.

**A. Analysis of Spatial and Temporal Variability of Stratospheric Trace Constituents and Temperatures**

**B. Principal Investigator:** Jack A. Kaye\*  
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**C. Research Objectives**

The objectives of this research are to understand from both data analysis and modeling perspectives the variability of trace constituents in the stratosphere and upper troposphere. Model calculations use the Goddard three-dimensional chemistry/transport model (R. B. Rood, PI) together with winds from the GSFC STRATAN data assimilation system. Data analysis includes data from satellite-, aircraft-, balloon-, and ground-based measurements. Emphasis is on how short-term meteorological variability affects the spatial and temporal distribution of trace constituents and their interrelationships.

**D. Progress**

There was major success in the studies of the short-term variability of hydrogen halides in the stratosphere using the 3-D model. Data were compared with column amounts of HCl and HF measured from the DC-8 during the Airborne Arctic Stratospheric Expedition (AASE) in 1989. Model calculations were also used to help understand how HCl and HF columns might be expected to correlate with meteorological parameters and how HCl amounts would be affected by removal on the surface of polar stratospheric cloud particles. The 3-D model calculations were used to help provide guidance as to the presence or absence of chemically processed air in specific geographic locations which might be sampled in future aircraft missions. Individual measurements of HCl and HF column amounts measured by R. Zander and co-workers from Jungfraujoch, Switzerland were obtained to help provide data to which modeled relationships between meteorological parameters and HCl and HF column amounts could be compared.

Two-dimensional model calculations of the distribution of fluorine-containing reservoir compounds in the stratosphere were carried out in conjunction with C. Jackman of NASA/GSFC. These calculations included the molecules CFCIO and CF<sub>2</sub>O, which were not normally considered in 2-D model calculations. The results of these calculations would lead to improved initial conditions for HF distributions in the 3-D chemistry/transport model.

Meteorological data from the National Meteorological Center (NMC) were also reexamined to help remove problems associated with previous analyses. Improved data products were prepared. Time series of derived quantities were prepared for use in looking at potential sites for stations in the Network for Detection of Stratospheric Change as well as for better characterizing potential vorticity at high northern latitudes. Software for easy analysis of ozone profiles from the Stratosphere Aerosol and Gase Experiment (SAGE-II) instrument was developed.

Research in the area of chemistry of isotopically substituted and vibrationally excited molecules in the Earth's upper atmosphere was also carried out.

### E. Recent Publications

- Kaye, J. A., Nonlocal thermodynamic equilibrium effects in stratospheric HF by collisional energy transfer from electronically excited O<sub>2</sub> and implications for infrared remote sensing, *Appl. Opt.* 28, 4161-4166, 1989.
- Kaye, J. A., R. B. Rood, D. J. Allen, E. M. Larson, and C. H. Jackman, Three-dimensional simulation of spatial and temporal variability of stratospheric hydrogen chloride, *Geophys. Res. Lett.* 16, 1149-1152, 1989.
- Kaye, J. A., and R. B. Rood, Simulations of short-term variability of stratospheric trace constituents, in *Our Changing Atmosphere, Proc. 28th Liege International Astrophysical Colloquium, June 26-30, 1989*, eds. P. Crutzen, J.-C. Gerard, and R. Zander, Universite de Liege, Cointe-Ougree, Belgium, 1989.
- Kaye, J. A., Stable isotopes as probes of changing atmospheric composition, in *Our Changing Atmosphere, Proc. 28th Liege International Astrophysical Colloquium, June 26-30, 1989*, eds. P. Crutzen, J.-C. Gerard, and R. Zander, Universite de Liege, Cointe-Ougree, Belgium, 1989.
- Kaye, J. A., Analysis of the origins and implications of the <sup>18</sup>O content of stratospheric water vapor, *J. Atmos. Chem.* 10, 39-57, 1990.
- Kaye, J. A., A. R. Douglass, R. B. Rood, R. S. Stolarski, P. A. Newman, D. J. Allen, E. M. Larson, M. T. Coffey, W. G. Mankin, and G. C. Toon, Three dimensional simulation of hydrogen chloride and hydrogen fluoride during the Airborne Arctic Stratospheric Expedition, *Geophys. Res. Lett.* 17, 529-532, 1990.
- Kaye, J. A., and C. H. Jackman, Comment on "Detection of Multiply Deuterated Methane in the Atmosphere," *Geophys. Res. Lett.*, 17, 659-660, 1990.
- Kaye, J. A., A. R. Douglass, R. B. Rood, R. S. Stolarski, P. A. Newman, D. J. Allen, and E. M. Larson, Spatial and temporal variability of the extent of chemically processed stratospheric air, *Geophys. Res. Lett.* 18, 29032, 1991.
- Kaye, J. A., A. R. Douglass, C. H. Jackman, R. S. Stolarski, R. Zander, and G. Roland, Two-dimensional model calculation of fluorine-containing reservoir species in the stratosphere, *J. Geophys. Res.* 96, 12,865-12,881, 1991.

## Three-Dimensional Modeling of Tropospheric Trace Gases.

Michael B. McElroy, Steven C. Wofsy, Daniel J. Jacob and Jennifer A. Logan

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### Abstract of Research Objectives.

Our program of research is designed to investigate quantitatively the factors that regulate the global and regional distributions of CO, NO<sub>x</sub>, NO<sub>y</sub>, and ozone in the troposphere. This work involves climatological simulations using a three dimensional chemical tracer model (CTM) based on meteorological information from the NASA/GISS general circulation model (GCM). Chemical transformations are computed with a parameterization scheme that retains the accuracy (within 10%) of a detailed photochemical mechanism. A major goal of our work is an assessment of the effects of human activity on atmospheric composition.

### Summary of Progress and Results.

Major features of transport in the CTM have been evaluated by our earlier studies of CFCs, <sup>85</sup>Kr, and <sup>222</sup>Rn, and the accuracy of the model's OH field has been tested by observations of CH<sub>3</sub>CCl<sub>3</sub>. Our recent focus has been carbon monoxide. We first developed a global inventory for CO with spatial resolution of 1°x1° for sources from combustion of fossil fuel, wood fuel, isoprene oxidation and biomass burning. The source from methane oxidation depends on OH and hence on CO itself, so it is calculated within the CTM during the run, using the parameterized chemistry for OH, and specified distributions for ozone, NO<sub>x</sub>, and CH<sub>4</sub>.

We have used our inventory in the CTM to predict the global distribution of CO. We find that the CTM reproduces major features of the CO distribution, such as the annual cycles observed at a variety of surface sites, latitudinal and vertical gradients implied by aircraft surveys, and longitudinal gradients and spatial patterns seen by the MAPS instrument on the Space Shuttle. While there are some minor discrepancies between model and observation, the overall quality of the agreement is very good. This suggests that the CO inventory must be reasonably accurate, since the sink for CO (removal by OH) is constrained by results from our earlier study of CH<sub>3</sub>CCl<sub>3</sub> that used the observed distribution of CO. Our analysis of the OH field in the model using data for CH<sub>3</sub>CCl<sub>3</sub> shows that global average values for OH are too high by only ~15%.

We have obtained quantitative constraints on our estimates of the two anthropogenic sources of CO, fossil fuel combustion and biomass burning, with a variety of sensitivity studies. This approach is possible because (1) estimates for the CO sink and the methane oxidation source are self-consistent, and are determined by OH, and (2) the remaining major sources, fossil fuel use and biomass burning, are located in geographically distinct regions. We find that our estimates of the anthropogenic sources should be reliable to ±25%. This constraint is particularly valuable for the source from biomass burning, because of the inherent difficulties in estimating the factors on which this source depends, such as areas and amount of vegetation burned.

Our CTM simulations show that the anthropogenic sources of CO are important on a global scale, even though the lifetime of CO is less than two months. Omitting the source from fossil/wood fuel burning reduces CO in the northern hemisphere by as much as a factor of 3, and even reduces CO at southern mid-latitudes by 15%, a consequence in part of the importance of transport from the north in supplying CO to this latitude belt. The source from biomass burning exerts its largest influence in the tropics and southern mid-latitudes, although its effect at northern mid-latitudes is by no means trivial; CO values there are lower by ~20% without this source. Omission of biomass burning reduces CO in the tropics and southern hemisphere by 30-50%, with largest reductions during the burning season. The amplitude of the annual cycle is considerably diminished, and maximum values occur 1-2 months earlier.

It appears that biomass burning is an important factor in determining the seasonal cycle of CO throughout the southern hemisphere. Tropical biomass burning has such a strong influence at southern mid-latitudes because the major local source, methane oxidation, is at a minimum in winter and early spring, and transport from the southern tropics is at a maximum. There is no significant annual cycle in the main source of CO at northern mid-latitudes, fossil fuel combustion, and here the annual cycle in CO is influenced by both the annual cycle in OH, and by that in transport.

Our 3-D study of CO shows that the effects of human activity on CO are global in nature. Nowhere on Earth can be regarded as pristine.

#### Publications.

- Balkanski, Y.J., and D.J. Jacob, Transport of continental air to the subantarctic Indian Ocean, *Tellus*, 42, 62-75, 1990.
- Balkanski, Y.J., D.J. Jacob, R. Arimoto, and M.A. Kritz, Long-range transport of radon-222 over the North Pacific Ocean, *J. Atmos. Chem.*, in review, 1991.
- Jacob, D.J., and M.J. Prather, Radon-222 as a test of convection in a general circulation model, *Tellus*, 42, 118-134, 1990.
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- Lacis, A.A., D.J. Wuebbles and J. A. Logan, Radiative forcing of global climate by changes in the vertical distribution of ozone, *J. Geophys. Res.*, 95, 9971-9981, 1990.
- Prather M. J., and C. M. Spivakovsky, Tropospheric OH and the lifetimes of hydrochlorofluorocarbons, *J. Geophys. Res.*, 95, 18,723-18729, 1990.
- Spivakovsky, C.M., S.C. Wofsy, and M.J. Prather, A numerical method for parameterization of atmospheric chemistry: computation of tropospheric OH, *J. Geophys. Res.*, 95, 18,433-18,440, 1990.
- Spivakovsky, C.M., R. Yevich, J.A. Logan, S.C. Wofsy, and M.B. McElroy, Tropospheric OH in a three dimensional chemical tracer model: an assessment based on observations of CH<sub>3</sub>CCl<sub>3</sub>, *J. Geophys. Res.*, 95, 18,441-18,471, 1990.

**A. Stratospheric Chemistry and Transport**

**B. Dr. Michael Prather, NASA, Goddard Institute for Space Studies, NY**

**C. Research Objectives**

The primary research goals of this project were to continue to develop the chemistry modules for the 3-D general circulation model of the middle atmosphere being developed by Dr. David Rind (GISS) under another task. The chemical tracer model (CTM) uses the wind fields from the GCM and applies the observed trace-gas climatologies of the stratosphere as a critical test of both the chemical model and the circulation of the GCM. A second objective under this task was to support the Upper Atmosphere Research Program's goals in assessing stratospheric ozone, both for the Congressionally mandated reports and the international assessments as part of the Montreal Protocol.

**D. Progress and Results**

A study of the Antarctic ozone hole with a 3-D chemical transport model (CTM) using a linearized photochemistry for ozone has been published. Studies of the N<sub>2</sub>O climatology predicted by the model have been completed, but are not yet submitted for publication. Parallel work on the study of small-scale chemical mixing was published; this work examined the importance of details of the mixing of the highly perturbed polar air as the winter polar vortex is eroded in the spring. A conclusion from the two studies is that chemical propagation of the Antarctic ozone hole occurs in two phases: rapid loss of ozone over the poles followed by dilution of this ozone poor air into mid latitudes, and, additionally, in the heterogeneously processed parcels spun out to mid latitudes as they evolve in isolation before final mixing with the background.

A significant effort during this period was spent supporting the ozone assessments. This work included reviews of stratospheric ozone modeling for the United Nations Environmental Programme's scientific panels and for Congressional Reports by NASA. In the course of these programmatic contributions, new research topics related to ozone assessments were discovered and published: an assessment of future ozone changes through modeling the chlorine and bromine loading of the atmosphere (Prather and Watson, 1990); an assessment of the environmental impacts of the Space Shuttle (Prather et al., 1990).

## E. Publications:

Prather, M., M.M. Garcia, R. Suozzo and D. Rind, Global impact of the Antarctic ozone hole: dynamical dilution with a 3-D chemical transport model, *J. Geophys. Res.*, 95, 3449-3471, (1990).

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Rind, D., R. Suozzo, N.K. Balachandran & M.J. Prather, Climate change and the middle atmosphere, part 1, the doubled CO<sub>2</sub> climate, *J. Atmos. Sci.*, 47, 475-494, (1990).

Prather, M.J. and R.T. Watson, Stratospheric ozone depletion and future levels of atmospheric chlorine and bromine, *Nature*, 334, 729-734, (1990).

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Watson, R.T., M.J. Kurylo, M.J. Prather and F.M. Ormond, Present state of knowledge of the upper atmosphere 1990: an assessment report (to Congress), NASA Reference Publication 1242, 208 pp, (1990).

[co-author of] Theory and observations: model simulations of the period 1955-1985, Chapter 7, **International Ozone Trends Panel Report**, World Meteorological Organization, Global Ozone Research and Monitoring Project, Report No. 18, (1990).

[co-author of] Model Predictions, Chapter 3, **Scientific Assessment of Stratospheric Ozone: 1989**, World Meteorological Organization, Global Ozone Research and Monitoring Project, Report No. 20, (1990).



**A. Chemical Transport Models for the Global Troposphere**

**B. Dr. Michael Prather, NASA, Goddard Institute for Space Studies, NY**

**C. Research Objectives**

This research is directed toward the continued development and application of a 3-D chemical transport model (CTM). The CTM has been developed at the Goddard Institute for Space Studies and Harvard University and is derived from the GISS general circulation model (GCM). The Harvard group's research effort is complementary and is presented in a separate NASA proposal. The GISS work focuses on three specific topics: (1) the interplay between sources, atmospheric transport, and chemical losses in determining the abundances of a trace gases observed at specific sites; (2) the role of convection in the global redistribution of chemical tracers; and (3) use of forecast or analyzed wind fields in a CTM.

**D. Progress and Results**

The GISS/Harvard CTM has been used in more than ten studies of tropospheric chemistry and tracer transport since 1987. The CTM has been applied recently to the study of the global distribution of  $\text{CH}_3\text{CCl}_3$  and  $\text{CH}_4$  (Spivakovsky et al., 1990; Fung et al., 1991), using static OH fields. These OH fields will be applied to the short-lived HCFCs (hydrochlorofluorocarbons) that are being considered as alternatives to the CFCs (chlorofluorocarbons). Some of the HCFCs have lifetimes so short (<2 yr) that chemical time scales are comparable to those for atmospheric transport. Preliminary results show that, under certain circumstances, uncertainties in the location of sources could be confused with an error in the lifetime of the gas. The development of a CTM using analyzed or forecast wind fields is in collaboration with I.S.A. Isaksen (U. Oslo) through a Norwegian research project being established at the European Centre for Medium Range Weather Forecasts (ECMWF). Preliminary meeting at ECMWF have already taken place.

**E. Publications:**

Spivakovsky, C.M., S.C. Wofsy and M.J. Prather, A numerical method for parameterization of atmospheric photochemistry: computation of tropospheric OH, J. Geophys. Res., 95, 18,433-18,439, (1990).

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Fung, I., J. John, J. Lerner, E. Matthews, M. Prather, L.P. Steele and P.J. Fraser, Three-Dimensional Model Synthesis of the Global Methane Cycle, J. Geophys. Res., 96, 13,033-13,065, (1991).

**A. Interpretation of In-situ and Satellite Trace Gas and Aerosol Data using Chemical-Dynamical Models**

**B. Principal Investigator**

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**C. Research Objectives**

This is a theoretical research project aimed at: (a) development of inverse methods which use a 3D model for determining regional and global source and sink strengths for long-lived trace gases important in ozone depletion and the greenhouse effect, (b) computation of the lifetimes and spatially resolved destruction rates of these gases using a 3D model, and (c) studies of the stratospheric sulfur cycle using a 3D model. The project uses and helps interpret certain satellite and in situ data sets. The satellite data of interest come from NIMBUS-7 (SAMS, SAM II, LIMS), SAGE-1 and SME. The in situ data come from balloons, aircraft, and ground-based observations (including in particular the Global Atmospheric Gases Experiment - GAGE). Important ultimate goals include determination of regional sources strengths of methane and also halocarbons restricted by the "Montreal Protocol", improvement in the accuracy of determination of the average tropospheric OH concentration using  $\text{CH}_3\text{CCl}_3$  data, determination of the lifetimes and regions of destruction of hydrohalocarbons proposed as alternatives to the above restricted halocarbons, and elucidation of the sources of stratospheric sulfate aerosols during volcanically perturbed times.

**D. Summary of Progress and Results**

We have recently completed runs of our global 3D chemical-dynamical model using updated rate constants and ultraviolet absorption coefficients for several trace gas reactions and species. We compute the present day and steady-state lifetimes of  $\text{CFCl}_3$  to be 46 and 42 years respectively, of  $\text{CF}_2\text{Cl}_2$  to be 124 and 107 years respectively, of  $\text{CF}_2\text{ClCFCl}_2$  to be 110 and 79 years respectively, of  $\text{CCl}_4$  to be 31 and 30 years respectively, and of  $\text{N}_2\text{O}$  to be 132 and 124 years respectively. These lifetimes were calculated to aid in the ongoing Environmental Assessments for stratospheric ozone depletion and greenhouse warming. In collaboration with NCAR we have carried out simulations of  $\text{CFCl}_3$  in the NCAR CCM2/T42 global general circulation model and compared these with ALE/GAGE  $\text{CFCl}_3$  data. This work is in preparation for the use of this three-dimensional model in an inverse process to determine the regional source strengths of trace gases (e.g.  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ) from global network measurements. Two papers describing 3D calculations for selected hydrochlorofluorocarbons have been published but we are now in the process of reassessing these calculations in view of the new lifetime for the hydrochlorocarbon  $\text{CH}_3\text{CCl}_3$  of 5.7 years recently deduced from twelve years of ALE/GAGE data.

**E. Publications**

R. Prinn and A. Golombek, 1990. Global atmospheric chemistry of CFC-123. *Nature*, **344**, 47-49.

A. Golombek and R. Prinn, 1989. Global three-dimensional calculations of the budget and present-day atmospheric lifetimes of  $\text{CF}_2\text{ClCFCl}_2$  (CFC-113) and  $\text{CHClF}_2$  (CFC-22). *Geophys. Res. Lett.*, **16**, 1153-1156.

R. Prinn, 1991. Global Atmospheric Chemistry and Global Pollution. In *"Energy and the Environment in the 21st Century"* (MIT Press, Cambridge, ed. J. Tester, D. Wood, N. Ferrari), p. 27-39.

R. Prinn, 1991. Tropospheric chemical models. In *"Proceedings of the 1990 Enrico Fermi International School of Physics"* (Il Nuovo Cimento, Rome, ed. G. Visconti), in press.

R. Prinn and D. Hartley, 1991. Atmosphere, ocean, and land: critical gaps in Earth System models. In *"Proceedings of the 1990 Global Change Institute on Earth System modelling"* (UCAR, Boulder, eds. D. Ojima, D. Schimel), in press.

A. TITLE:  
MODELLING THE EFFECTS OF CLIMATE CHANGE ON THE MIDDLE ATMOSPHERE

B. INVESTIGATORS / INSTITUTION  
DAVID RIND / NASA GODDARD INSTITUTE FOR SPACE STUDIES

C. ABSTRACT OF RESEARCH OBJECTIVES

The proposed objective of this research is to understand how climate change can effect the stratosphere and tropospheric/stratospheric interactions and exchanges. A three-dimensional general circulation model extending from the surface to 85 km altitude is used to simulate the climate of the troposphere/middle atmosphere with various climate perturbations, such as increased levels of CO<sub>2</sub>, volcanic aerosols, and solar perturbations. Of interest is how the climate change affects the radiative and dynamical characteristics of the stratosphere and troposphere, and troposphere/stratosphere exchanges. The winds and fluxes generated by the model are saved off-line for use with a chemical tracer model, which, as part of a separate investigation, characterizes the impact of climate change on various trace gas species

D. SUMMARY OF PROGRESS AND RESULTS (1990, 1991)

The impact of doubled CO<sub>2</sub> on the troposphere/middle atmosphere system was investigated in a series of runs (Rind et al., 1990). The troposphere warmed by up to 10°C, and the stratosphere cooled, in general. This decreased the vertical stability of the atmosphere, increased planetary long wave generation in the troposphere, and, in conjunction with altered tropospheric winds, allowed more wave energy to propagate into the stratosphere. Convergence of this wave energy accelerated the stratospheric circulation by 10-20%.

These results imply that in the doubled CO<sub>2</sub> climate, trace gases may be transferred into the stratosphere in the tropics, and from the stratosphere into the troposphere in the extratropics, at an accelerated rate. The distribution of ozone in the stratosphere would also be changed by both the increased residual circulation and the greater eddy amplitudes.

The effect of volcanic aerosols on the troposphere/middle atmosphere was explored in the next set of experiments (Rind et al., 1991). Two sets of simulations were run, the first in which the aerosols remained in the atmosphere for only three years (similar to recent large volcanoes), and the second in which the aerosols were given time to cool the oceans fully (on the order of 50 years).

In the experiment with the short aerosol residence time, the lower stratosphere warmed by several degrees, which reduced the static stability of the tropical atmosphere. A resultant decrease in Hadley Circulation and low latitude rainfall occurred, along with an increase in subtropical rainfall, mid latitude standing wave energy, and energy flux into the stratosphere (all factors which seemed to arise after the eruption of Mt. Agung in 1963). The circulation in the stratosphere was affected, which helped produce cooling in the polar lower stratosphere and tropical stratopause, and warming at the polar stratopause (and again, some of these features were observed after Mt. Agung and El Chichon).

In the experiment in which the oceans were allowed to fully adjust, substantial differences occurred between the response of the

Southern and Northern Hemisphere middle atmosphere circulations. The N.H. circulation weakened, and the S.H. circulation strengthened, a direct result of the difference in sea ice response, latitudinal temperature gradient, and eddy energy generation in their respective tropospheres. These sets of experiments emphasize the interactive nature of the middle atmosphere/climate system.

The next set of experiments is focusing on the impact of the quasi-biennial oscillation (QBO) and solar forcing. Specified drag was input to the tropical lower stratosphere, producing either tropical east winds or tropical westerlies. The subsequent development of the stratosphere was then monitored; with tropical east winds a major warming developed, but not with tropical west winds (in agreement with observations for low solar activity). The response was the result of variation in planetary wave propagation from the troposphere (Balachandran et al., 1991). The impact of the QBO on forcing of the Antarctic ozone hole region is being investigated in a separate study.

Experiments have now begun varying the solar ultraviolet radiation, as occurs during the solar sunspot cycle. These are being done in conjunction with the QBO experiments to explore whether the correlations noted in the literature can be reproduced, a test of both coupled troposphere/stratosphere models and the validity of the empirical relationships.

Model development is continuing with the implementation of a finer resolution model, now possible due to recent increases in computer power. The ultimate aim is to couple the dynamic model with the photochemical model being employed by Prather et al.

#### E. JOURNAL PUBLICATIONS

Rind, D., Suozzo, R., Balachandran, N.K. and M.J. Prather, 1990: Climate change and the middle atmosphere. Part I: The doubled CO<sub>2</sub> climate. J. Atmos. Sci., 47, 475-494, 1990.

Rind, D., Balachandran, N.K. and R. Suozzo, 1991: Climate change and the middle atmosphere. Part II: The impact of volcanic aerosols. J. Climate, in press.

Balachandran, N.K., Plumb, A., Suozzo, R., and Rind, D., 1991: The QBO and stratospheric warming - model results. JGG, in press.

Rind, D. and A. Lacis, 1991: The role of the stratosphere in climate change. Submitted to Rev. Geophys.

**A. Studies of the Antarctic Ozone Hole: Analysis of Perturbations to Global Ozone Trends**

**B. Principal Investigators:** Jose M. Rodriguez, Malcolm K. W. Ko and Nien Dak Sze

**Co-investigator:** Debra K. Weisenstein, all at Atmospheric and Environmental Research, Inc., 840 Memorial Drive, Cambridge, MA 02139

**C. Abstract of Research Objective**

The general objective of this program is to refine our understanding of the chemistry of the antarctic ozone hole, and to study the impact of polar phenomena (heterogeneous chemistry, dilution effect, denitrification) on the global ozone trends. The specific goals are:

- Further studies of the dilution of the antarctic ozone loss using our two-dimensional chemistry transport model; comparison to other model results and observational data.
- Incorporation of heterogeneous processes into our 2-D model, both in the polar regions and in the global atmosphere, in a manner consistent with available laboratory data and field measurements.
- Assessment of the impact of heterogeneous reactions both for the present and future atmosphere; assessment of the future behavior of the antarctic ozone hole and its impact on global ozone trends; assessment of the coupling among ozone and temperature perturbations, circulation changes, and dynamical redistribution.

**D. Summary of Progress and Results**

**Implications of New Kinetic Data for the Analysis of Ozone Loss in Antarctica**

We concluded our analysis of the role of chlorine in the observed ozone loss during Antarctic spring, in light of new formation and photolysis rates for  $\text{Cl}_2\text{O}_2$ . Our analysis calculated the partitioning between different chlorine species both in the edge and towards the center of the vortex, taking into account both the *in-situ* measurements of  $\text{ClO}$ , and the observed decrease in column densities of  $\text{HCl}$  and  $\text{ClNO}_3$  towards the center of the vortex. With this constraint, our calculated ozone reductions could account for about 75% of the observed ozone decrease at  $70^\circ\text{S}$ , and about 100% of the observed decrease at  $80^\circ$ . Given uncertainties in kinetics and air parcel trajectories, our analysis did not indicate the need for further mechanisms to explain the antarctic ozone depletion, although remaining uncertainties could indeed accommodate other processes. Results were published in Rodriguez et al., 1990. Revisions of the  $\text{ClO}$  data after publication of this paper improved the agreement between model calculations and data and supported our conclusions.

**Early Detection of Stratospheric Change**

We carried out calculations of expected temporal and spatial signatures of different heterogeneous mechanisms on species to be measured by the Network for the Detection of Stratospheric Change (NDSC). Our calculations indicated that the largest signatures would occur for reactions involving  $\text{ClNO}_3$  with water and/or  $\text{HCl}$ . Although our calculations have indicated latitudinal, seasonal and decadal signatures of heterogeneous chemistry, many of these signatures could fall within observational uncertainty of the natural variability of the atmosphere. A concerted set of measurements at different locations and seasons, particularly high winter latitudes, could elucidate the occurrence of heterogeneous processes. The largest signatures would be observable in the trends of column  $\text{OCIO}$ , and in the latitudinal gradients of column  $\text{OCIO}$ ,  $\text{ClO}$ ,  $\text{ClNO}_3$  and  $\text{NO}_2$ . Our results have been

made available to the Steering Committee of the NDSC (Kurylo and Solomon, 1990) <sup>1</sup> for planning purposes.

#### Heterogeneous Chemistry on Sulfate Aerosols

Measurements of the reaction efficiency of  $\text{N}_2\text{O}_5$  on sulfuric acid solutions have indicated values, of order 0.1. Furthermore, these values seem fairly independent of the water content of the sulfuric acid solution, in contrast to those obtained for reactions involving  $\text{ClNO}_3$ . We have incorporated into our 2-D model the reaction of  $\text{N}_2\text{O}_5$  occurring on the global sulfate aerosol layer at all latitudes and seasons. Calculated ozone trends between 1980 and 1990 increase by almost a factor of two after inclusion of this reaction, even at mid-latitudes (Rodriguez et al 1991). These results are in closer agreement with trends derived from Dobson and satellite data. Inclusion of this reaction into the model also indicates signatures in the concentrations of  $\text{ClO}$ ,  $\text{NO}_x$  and  $\text{OH}$  which should be observable in atmospheric measurements. The chemistry scheme has been applied to study the impact on ozone from  $\text{NO}_x$  emitted by stratospheric aircraft. (Weisenstein et al 1991).

#### Studies of the Ozone Budget

Incorporation of heterogeneous conversion of  $\text{N}_2\text{O}_5$  to  $\text{HNO}_3$  on sulfate aerosols dramatically reduces the calculated concentrations of  $\text{NO}_x$  in the lower stratosphere, and increases the calculated abundances of  $\text{OH}$  and  $\text{ClO}$ . As a result, our understanding of the catalytic processes which remove ozone in this region changes substantially: whether in models with only gas-phase chemistry over half of the ozone removal occurs through  $\text{NO}_x$ -mediated processes, most of the ozone removal occurs through  $\text{HO}_x$  and  $\text{Cl}_x$ -mediated mechanisms in models including the above heterogeneous conversion. Work is in progress to study the implications of the above to the calculated ozone response to perturbations in  $\text{NO}_x$ ,  $\text{Cl}_x$  and  $\text{HO}_x$  in the lower stratosphere.

#### E. Publications

Rodriguez, J. M., M. K. W. Ko, and N. D. Sze (1990) The role of chlorine chemistry in Antarctic ozone loss: Implications of new kinetic data. *Geophys. Res. Lett.*, **17**, 255-258.

Rodriguez, J. M., M. K. W. Ko, and N. D. Sze (1991) Role of heterogeneous conversion of  $\text{N}_2\text{O}_5$  on sulphate aerosols in global ozone losses. *Nature*, **352**, 134-137.

#### Publications in Preparation

Rodriguez, J. M., M. K. W. Ko, D. K. Weisenstein and N. D. Sze (1991) Ozone budget in the lower stratosphere: Impact of heterogeneous chemistry.

Weisenstein, D. K., M. K. W. Ko, J. M. Rodriguez and N. D. Sze (1991) Impact of heterogeneous chemistry on model-calculated ozone change due to HSCT aircraft. Submitted to *Geophys. Res. Lett.*

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<sup>1</sup> Kurylo, M.J. and S. Solomon, Network for the Detection of Stratospheric Change, A Status and Implementation Report, NASA, Jan. 1990.



**A. Utilization of Stratospheric Data in 2-D Model Studies of the Photochemistry, Interannual Variability and Spatial Distribution of Trace Gases**

**B. Principal Investigators:** Jose M. Rodriguez, Hans R. Schneider and Run-Li Shia

**Co-Investigators:** Malcolm K. W. Ko, Song M. Fan, Curtis W. Heisey and Nien Dak Sze, all at Atmospheric and Environmental Research, Inc., 840 Memorial Drive, Cambridge, MA 02139

**C. Abstract of Research Objective**

The purpose of the proposed research is to acquire and incorporate satellite and aircraft data into the AER 2-D model in an effort to address outstanding issues relating to the role of heterogeneous chemistry, transport, and other processes controlling the interannual variability and latitudinal distribution of ozone and other trace species. The main objectives of the proposed research are: validation of present photochemical schemes; realistic parameterization of heterogeneous chemistry in terms of laboratory data and aerosol observations; determination of the interannual and latitudinal variability of heterogeneous chemistry; assessment of the role of dilution, heterogeneous chemistry, dynamics, and  $\text{NO}_2$  in the observed trends of ozone; and simulation of the latitudinal variation of different constituents.

**D. Summary of Progress and Results**

**Acquisition of Data**

We have acquired the final data from the AAOE and AASE campaigns, and merged into a common file with uniform time grid for easy usage. We have also acquired the latest version of TOMS (Version 6), and are presently using these data to estimate expected changes in solar UV at the ground caused by the observed ozone changes, and refining the impact of ozone dilution on the ozone trends in the Southern hemisphere. Representative measurements of  $\text{NO}_2$  and aerosols by SAGE-II have been provided to us by the group at NASA/Langley. These measurements are being used to determine possible signatures of heterogeneous processes, and to estimate the spatial and temporal extent of heterogeneous reactions which are sensitive to aerosol water content. Finally, we have also acquired the STEP Data.

**Analysis of SME Data**

Work has continued on the analysis of ozone and solar UV data obtained by the SME instrument, in order to determine a signature of short-term variability of solar output in the ozone measurements. Statistically significant correlations between ozone and solar UV variations are obtained at altitudes between 50 and 80 km. We have also calculated the expected variability by forcing a 1-D model of the mesosphere with the SME solar UV as input, and find that the calculated response of the model is consistent with observations.

**Analysis of  $\text{N}_2\text{O}$  from the SAMS Instrument**

We concluded our analysis of these data in order to determine budgets and lifetimes of  $\text{N}_2\text{O}$ , and implications for other trace gases. We calculate that 80% of the  $\text{N}_2\text{O}$  is removed in the stratosphere between  $30^\circ\text{N}$  and  $30^\circ\text{S}$ . Analysis of the SAMS data indicates that previous models may have underestimated the magnitude of vertical transport over the tropics, and the calculated lifetimes for  $\text{N}_2\text{O}$  (110 years) and CFCs (47 years for CFC-11 and 90 years for CFC-12) could be 30% shorter than previously reported values. Shorter lifetimes for CFCs would imply a more rapid decrease in the atmospheric chlorine content once the CFC emissions are stopped, making it possible to reach pre-ozone hole values of 2ppbv as early as 2045.

### Interannual Variation of Ozone

We concluded our analysis of four years of monthly mean ozone data and NMC temperature. Our analysis suggested that the observed interannual variability in ozone is a response to fluctuations in the transport circulation in the lower stratosphere. We also performed sensitivity studies to check any dependence on details of the heating calculation, the choice of eddy diffusion coefficients, the method of interpolating ozone onto our model grid, and the choice of latitude bands for comparison. Results of this study have appeared in Schneider et al., 1991 (see below).

### Interannual Variation in the Frequency of Polar Stratospheric Clouds in Antarctica

Recent analysis of the SAM-II data indicate that the frequency of observations of PSCs over Antarctica correlates with the phase of the quasi-biennial oscillation (QBO), with larger frequencies of sightings coinciding with years of westerly phase. We have simulated the effect from heterogeneous chemistry triggered by the occurrence of PSCs in our photochemical model by turning on and off the heterogeneous chemistry according to the observed frequencies. Although we do obtain larger rates of ozone depletion in the years with larger frequency of PSCs, the magnitude of the inter-annual oscillations induced by changes in the heterogeneous chemistry is not as large as observed in the ozone data. These results suggest that modulation of heterogeneous chemistry by PSCs alone cannot account for the observed interannual changes in the rate of decline of antarctic ozone. Other processes (dynamics, denitrification) may also play an important role.

### Utilization of ATMOS Data

Results of our 2-D model have been provided to members of the ATMOS team for further comparison of their measurements with model calculations. These results will also be utilized for planning of the future ATLAS mission.

### E. Publications

Ko, M.K.W., N.D. Sze and D.K. Weisenstein (1991) Use of satellite data to constrain model calculated atmospheric lifetimes for N<sub>2</sub>O and the CFCs. *J. Geophys. Res.*, **95**, 7547-7552.

Schneider, H. R., M. K. W. Ko, C. A. Peterson and E. Nash (1991) Interannual variations of ozone: Interpretation of 4 years of satellite observations of total ozone. *J. Geophys. Res.*, **96**, 2889-2896.

### Publications in Preparation

Fan, S. M., J. M. Rodriguez, M. K. W. Ko, and N. D. Sze (1991) Short-term variability of mesospheric ozone as observed in SME data: Analysis of observations and modeling results. To be submitted to *Planetary and Space Science*

Heisey, C. W., J. M. Rodriguez, M. K. W. Ko and N. D. Sze (1991) The interannual variation in the evolution of the Antarctic ozone hole.

**A. Zonally-averaged Model of Dynamics, Chemistry and Radiation for the Atmosphere**

**B. Principle Investigators:** Nien-Dak Sze and Malcolm Ko  
**Co-investigators:** Jose M. Rodriguez, Song-M. Fan, Hans Schneider, Run-Li Shia, and Debra K. Weisenstein, all at Atmospheric and Environmental Research, Inc., 840 Memorial Drive, Cambridge, MA 02139

**C. Abstract of Research Objective**

The overall goal of the project is to improve and better quantify our understanding of the processes that control the distribution and abundance of stratospheric ozone and its sensitivity to either natural or anthropogenic influences. The scientific objectives, which are designed around the two-dimensional zonal mean (2-D) modeling capability at AER, are:

- To assess the limitation of 2-D models, to refine and enhance our current (2-D) modeling capabilities and understanding of the stratosphere through model simulations and validation of model results using observed data.
- To develop an interactive 2-D model with interactive chemistry, dynamics and radiation.
- To assess the susceptibility of stratospheric ozone to natural and anthropogenic perturbations.

**D. Summary of Progress and Results**

**Model Validation and Comparison with Observation**

(Ko et al, 1990): By comparing the model calculated distribution of  $N_2O$  with the observation from the SAMS instrument on Nimbus-7, we concluded that previous models may have underestimated the strength of upwelling at the tropical lower stratosphere. A stronger upwelling would imply shorter atmospheric lifetimes for  $N_2O$ , CFC-11 and CFC-12.

(Weisenstein et al, 1991; Rinsland et al, 1990; Rinsland et al, 1991): Using historical and/or estimated emission rates of the halocarbons and  $SF_6$ , we calculated the time evolution of  $SF_6$ , F-22 and the chlorine content of the atmosphere and provided estimates for the contributions of each halocarbons to the chlorine loading and to  $COF_2$ . The model simulated behavior of HF and HCl is compared to the infrared measured abundances above Kitt Peak between 1977 and 1990.

(Plumb and Ko, 1991): Various studies have demonstrated that the concentrations of many trace gases measured in the same air-parcel in the lower stratosphere consistently show an almost linear dependence. We explained why this behavior is to be expected because of the transport characteristics in the lower stratosphere and suggested that a methodology could be developed to make use of existing data for model validation.

**Interactive 2-D Model**

(Schneider and Ko, 1989; Hou, Schneider and Ko, 1991): The 2-D interactive model with simplified chemistry is used to demonstrate that a smaller  $K_{yy}$  in the southern hemisphere causes a less poleward-extended circulation in the south, resulting in a sub-polar springtime maximum (rather than a polar maximum) in the ozone column abundance.

The 2-D interactive model with full chemistry is now operational. We used the model to simulate the present day atmosphere and perform a number of perturbation calculations. Our results showed that cooling of the stratosphere from  $CO_2$  could compensate for the ozone decreases due to increase in CFCs. Two manuscript are being prepared for publication.

**Assessment Calculations**

(Wang et al, 1990): We used the predicted ozone decrease from the AER 2-D photochemical model in the AER 2-D climate model to calculate the effect of ozone redistribution to greenhouse warming.

(Fisher et al, 1990): We used the AER 1-D and 2-D model to calculate the ozone depletion potentials and chlorine loading potentials of a number of CFCs, HCFCs and halons and compare our results with other modeling groups. These results are now being updated for the UNEP (1992) report using new laboratory kinetics data.

(Rodriguez et al, 1991; Fan et al, 1991): The lifetimes of the HCFCs and HFCs are determined by reactions with OH in the troposphere. We performed a number of studies to analyze the coupling between the CH<sub>4</sub>-CO-OH system as part of the overall effort to understand the behavior of tropospheric OH in the future atmosphere and how it may affect the HCFC and HFC lifetimes.

(Prather et al, 1990) : The 2-D model was used to assess the impact on ozone from chlorine release associated with space shuttle operation.

We performed a number of scenario calculations for the UNEP(1992) report.

## E. Publications

- Schneider, H.R., and M.K.W. Ko (1989) The response of an interactive 2-D model to ozone changes: an estimate of the radiative dynamical feedback effect. *J. Geophys. Res.*, **95**, 5657-5668.
- Wang, W.-C., G. Molnar, M.K.W. Ko, S. Goldenberg, and N.D. Sze (1990) Atmospheric trace gases and climate: a seasonal model study. *Tellus*, **42B**, 149-161.
- Fisher, D.A., C.H. Hales, D.L. Filkin, M.K.W. Ko, N.D. Sze, P.S. Connell, D.J. Wuebbles, I.S.A. Isaksen and F. Stordal (1990) Model calculations of the relative effects of CFCs and their replacements on stratospheric ozone. *Nature*, **344**, 508-512.
- Prather, M.J., M.M. Garcia, A.R. Douglass, C.H. Jackman, M.K.W. Ko, and N.D. Sze (1990) The space shuttle's impact on the stratosphere. *J. Geophys. Res.*, **95** (D11), 18,583-18,590.
- Rinsland, C.P., A. Goldman, F.J. Murcray, R.D. Blatherwick, J.J. Kusters, D.G. Murcray, N.D. Sze and S.T. Massie (1991) Long-term trends in the concentrations of SF<sub>6</sub>, CHClF<sub>2</sub>, and COF<sub>2</sub> in the lower stratosphere from analysis of higher-resolution infrared solar occultation spectra. *J. Geophys. Res.*, **95**, 16,477-16,490.
- Hou, A.Y., H.R. Schneider, and M.K.W. Ko (1991) A dynamical explanation for the asymmetry in zonally averaged column abundances of ozone between northern and southern springs. *J. Atmos. Sci.*, **48**, 547-556.
- Ko, M.K.W., N.D. Sze and D.K. Weisenstein (1991) Use of satellite data to constrain model calculated atmospheric lifetimes for N<sub>2</sub>O and the CFCs. *J. Geophys. Res.*, **95**, 7547-7552.
- Manuscripts under review and work in progress
- Weisenstein, D., M.K.W. Ko and N. D. Sze (1991) The chlorine budget of the present day atmosphere: A modeling study. Submitted to *J. Geophys. Res.*
- Plumb, A.R. and M.K.W. Ko (1991) Interrelationships between mixing ratios of long-lived stratospheric constituents. Submitted to *J. Geophys. Res.*
- Rinsland, C.P., J.S. Levine, R. Zander, A. Goldman, N.D. Sze, M.K.W. Ko, and D.W. Johnson (1991) Infrared measurements of HF and HCl total column abundances above Kitt Peak, 1977-1990: seasonal cycles, increases in total HF, total HCl, and the HF/HCl total columns ratio, and comparisons with two-dimensional model calculations. Submitted to *J. Geophys. Res.*
- Rodriguez, J.M., M.K.W. Ko, N.D. Sze and C.W. Heisey (1990) Impact of biomass burning on tropospheric CO and OH: A two-dimensional study. Proceedings of the Chapman Conference on Global Biomass Burning, May 1990, Charlottesville, VA.
- Fan, S.M., J.M. Rodriguez, M.K.W. Ko and N.D. Sze (1991) A time-dependent 2-dimensional model study of the trend in atmospheric methane. Proceedings of the International Symposium on Environmental Biogeochemistry, August 19-23, 1991, San Francisco, CA.
- Ko, M.K.W., H.R. Schneider, R.L. Shia, D.K. Weisenstein and N.D. Sze (1991) Simulation of the middle atmosphere by a two-dimensional model with coupled dynamics, radiative transfer and photochemistry.
- Schneider, H.R., M.K.W. Ko, R.L. Shia, D.K. Weisenstein and N.D. Sze (1991) Two-dimensional model assessment of the response of stratospheric Ozone to increased levels of CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub> and CFC's.

**NASA RESEARCH SUMMARY**  
**Grant No. NAGW-1605**

**A. Title of Research Task**

*Zonally averaged model of dynamics, chemistry and radiation for the atmosphere*

**B. Principle Investigator and Institution**

Ka-Kit Tung, Professor of Applied Mathematics, University of Washington, Seattle, WA 98195.

**C. Abstract of Research Objectives**

To simulate and understand the observed distribution of chemical species such as ozone, odd nitrogen and chlorine using a coupled model incorporating comprehensive chemistry, radiative transfer and physically based dynamical transport; to study the observed year-to-year variations of column ozone with the aid of the 2-D model; to enhance the capability of the 2-D model.

**D. Summary of Progress and Results**

Simulated result for the chemical composition of the stratosphere has been published. Very favorable comparison has been obtained. More recent work involves the use of the 2-D model to analyze long term trends in TOMS data, to devise parametrization for wave mixing to be used in a predictive version of the model, and to test and validate the tropospheric portion of the model. These tasks are in progress.

**E. Journal publications**

H. Yang, E.P. Olagner and K. K. Tung: Simulation of the present-day ozone, odd nitrogen, chlorine and other species using a coupled 2-D model in isentropic coordinates, *J. Atmospheric Sciences*, **48**, 442-471, 1991.

E.P. Olagner, H. Yang and K.K. Tung: A reexamination of the radiative balance of the stratosphere, *J. Atmospheric Sciences*, accepted, 1991.

H. Yang, K.K. Tung, and E. Olagner: Nongeostrophic theory of zonally averaged circulation. Part II: Eliassen-Palm flux divergence and isentropic mixing coefficient. *J. Atmospheric Sciences*. **47**, 215-241, 1990.

## Research Summary 1990-1991

### A. Title of Research Task

Interactions of Atmospheric Chemical, Radiative, and Dynamical Processes: Research Studies with and Further Development of the LLNL Two-Dimensional Global Atmospheric Model

### B. Investigators and Institutions

Principal Investigator: Dr. Donald J. Wuebbles  
Lawrence Livermore National Laboratory  
Livermore, CA 94550

Co-investigators: Dr. Peter Connell, Dr. Keith Grant, Dr. Douglas Kinnison,  
and Dr. Douglas Rotman

### C. Research Objectives

Research has primarily emphasized: (1) the further development of the LLNL two-dimensional chemical-radiative-transport model of the global atmosphere; and (2) research studies using this and other global atmospheric models to gain better understanding of the processes affecting the middle atmosphere, with emphasis on assessing past and possible future changes in ozone resulting from natural and human-induced causes.

### D. Progress and Results

We are in the process of largely redesigning the two-dimensional model, aimed at making the treatment of atmospheric dynamics and transport more interactive and self-consistent, expanding the treatment of atmospheric chemical processes, modularizing the code towards easier updates in the future, and making the model more computationally efficient by reconsidering the numerical solution algorithms. Additional chemistry for HCFCs, Halons and associated bromine reactions have been included in the model. Aerosol and polar stratospheric cloud (PSC) associated heterogeneous chemistry are currently being included into the 2-D model. We are revising our calculational procedure to one that solves the continuity, momentum and energy equations along with a consistent evaluation of the Eliassen-Palm flux divergence and the  $K_{yy}$  and  $K_{zz}$  representations used for the eddy transport of energy and species. We have also begun the development of a high resolution version of the model (to about 1.5 km in altitude and 5 degrees in latitude).

LLNL scientists have participated in several international assessment efforts in support of NASA's lead role in the preparation of these assessments. D.W. was a lead author of the chapter on radiative forcing for the 1990 IPCC assessment on climate change. We also provided model calculations for changes in atmospheric composition for the future emissions scenarios developed by the IPCC. D.W. is a lead author on the chapter of the new UNEP ozone assessment concerning Ozone Depletion Potentials. We are providing atmospheric model calculations for a number of the other chapters of the report.

Several research studies (Wuebbles and Kinnison, 1990; Kinnison and Wuebbles, 1991) have examined the potential effects of high-flying aircraft on stratospheric ozone. These papers suggest that current aircraft emissions may be affecting upper tropospheric ozone concentrations.

We have analyzed the effects of changes in the distribution of tropospheric and stratospheric ozone on radiative forcing of climate (Lacis et al., 1990). The study indicated that climate forcing is most responsive to changes in ozone in the upper troposphere and lower stratosphere.

The 2-D model was used in an analysis to examine the influence of solar variations and trace gas emissions on upper stratospheric ozone and temperature during the 1970s and 1980s (Wuebbles et al., 1991). In addition to determining the trends in ozone and temperature over this period, the model was also used to evaluate the effects of ultraviolet variations from solar maximum to solar minimum during the 11-year solar cycle. The

model calculations can adequately explain the observed trends in upper stratospheric ozone from 1979 to 1986. In a separate study using the 2-D model, we have also shown that the increase in ozone measured throughout the 1960s can largely be explained by a combination of the decrease in ozone expected from the NO<sub>x</sub> produced in the nuclear tests and the effects of the 11-year solar cycle variations (solar minimum was reached at the same time as the maximum effects of the nuclear tests on ozone in 1962-1963).

A series of sensitivity studies have been completed to examine model-calculated distributions of carbon-14 and strontium-90 based on the atmospheric nuclear tests (Kinnison, et al., 1991). The model-derived distribution of carbon-14 was quite sensitive to assumptions in treating lower stratospheric transport processes. The model-derived distribution of carbon-14 calculated by accounting for each individual nuclear test into the model produced a close representation of the observational database for carbon-14.

Diurnal variations of mid-stratospheric NO<sub>2</sub> derived from the 1-D model were used in an analysis to understand balloon measurements over France (Offermann et al., 1991).

We are completing a research study to comprehensively examine the replacements being considered for CFCs and Halons. We have determined the calculated lifetimes and ODPs for these alternatives. Temperature dependent cross-sections have been included in the model for this analysis. Studies are also underway to examine the sensitivity of lower stratospheric chemistry to heterogeneous chemical processes, including how this chemistry may affect ODP calculations and to what extent perturbations to ozone from chlorine and bromine emissions may be affected by these processes.

Miller et al. (1991) have examined the radiative effects of observed changes in lower stratospheric ozone and carbon dioxide over the last two decades as to whether these changes can explain the observed trends in lower stratospheric temperatures from rawinsonde data taken in the Northern midlatitudes. The derived temperature changes seem to generally match the magnitude and the shape of the observed trends.

## E. Publications

- Kinnison, D.E., and D.J. Wuebbles, Influence of present and possible future aircraft emissions on the global ozone distribution, LLNL report UCRL-JC-194677, 1990; also *AMS Symposium on Global Change Studies, American Met. Soc.*, Boston, MA, 1991.
- Kinnison, D.E., D.J. Wuebbles, and H.S. Johnston, Two dimensional model study of atmospheric transport using carbon-14 and strontium-90 as inert tracers," submitted to *J. Geophys. Res.*, 1991.
- Lacis, A.A., D.J. Wuebbles, and J.A. Logan, Radiative forcing of climate by changes in the vertical distribution of ozone, *J. Geophys. Res.*, 95, 9971-9981, 1990.
- Miller, A.J., R.M. Nagatani, G.C. Tiao, X.F. Niu, G.C. Reinsel, D. Wuebbles, and K. Grant, Comparisons of observed ozone and temperature trends in the lower stratosphere, submitted to *Geophys. Res. Lett.*, 1991.
- Offermann, D., M. Riese, C.P. DeBakker and D.J. Wuebbles, Stratospheric trace gas variability: A case study, *Planetary and Space Sci.*, in press, 1991.
- Tiao, G.C., G.C. Reinsel, D. Xu, J. H. Pedrick, X. Zhu, A.J. Miller, J.J. DeLuisi, C.L. Mateer and D.J. Wuebbles, Effects of autocorrelation and temporal sampling schemes on estimates of trend and spatial correlation, *J. Geophys. Res.* 95, 20507-20517, 1990.
- Wuebbles, D.J., and D.E. Kinnison, Solar variations and their influence on trends in upper stratospheric ozone and temperature, LLNL report UCRL-JC-106108, 1990; also *Second AMS Symposium on Global Change Studies, American Met. Soc.*, Boston, MA, 1991.
- Wuebbles, D.J., and D.E. Kinnison, Sensitivity of stratospheric ozone to present and possible future aircraft emissions, in *Air Traffic and the Environment — Background Tendencies and Potential Global Atmospheric Effects*, U. Schumann, editor, Springer-Verlag, Berlin, 1990.
- Wuebbles, D.J., D.E. Kinnison, K.E. Grant, and J. Lean, The effect of solar flux variations and trace gas emissions on recent trends in stratospheric ozone and temperature, *J. Geomagnetism and Geoelectricity*, in press, 1991.





#### IV. ASSESSMENTS, COORDINATION, MISCELLANEOUS

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# JANAF Thermochemical Tables for Species of Importance to Ozone Depletion

David B. Neumann, Malcolm W. Chase

National Institute of Standards and Technology  
Gaithersburg, MD

Models of the dynamics of stratospheric composition related to the ozone depletion problem require accurate geophysical, kinetic, as well as chemical thermodynamic data. The objective of the current study is to provide NASA with a comprehensive evaluation of the thermodynamic data for stable as well as transient species involved in the network of reactions related to the destruction of ozone in the upper atmosphere. Data evaluations and thermodynamic tables for the species ClO, OClO, ClOO, ClOCl, ClClO, (ClO)<sub>2</sub>, ClOClO<sub>2</sub>, and NO<sub>3</sub> were provided in FY1990. The set of gas phase species evaluated in FY1991 are:

OH, OH<sub>2</sub>, HCl, HOCl, HOClO, HOClO<sub>2</sub>, HOClO<sub>3</sub>, ClNO, ClNO<sub>2</sub>, ClONO, ClONO<sub>2</sub>

The evaluation process involves three steps: (1) compile annotated bibliographies containing the relevant references needed to obtain the thermodynamic properties of the species; (2) Extract the spectroscopic and thermodynamic data from the references, perform recalculations and adjustments of experimental values where necessary, and determine the final data to be used to calculate the thermodynamic tables; (3) Compute and document the thermochemical tables and distribute them to interested parties for comment to ensure their consistency with available knowledge.

At the present time the annotated bibliographies for the species have been assembled and the relevant data has been extracted for all the species of interest. Due to various reaction networks, or pathways, experimental thermodynamic data for a number of the species has been found to be closely related to the thermodynamic properties of the species evaluated in FY1990. Data summaries of the relevant thermodynamic and spectroscopic data have been written for eight of the eleven species under the current program. Computation of the thermodynamic tables for several of the species is now underway.

Summary versions of the thermodynamic tables in JANAF format for the eight species studied under the first part of this work have recently been published: Abramowitz, S.; Chase, M. W.; "Thermodynamic Properties of Gas Phase Species of Importance to Ozone Depletion"; Pure Applied Chem.; **63**, 1449-54 (1991). The complete tables with their documentation have been submitted for publication: Abramowitz, S.; Chase, M. W.; "Thermodynamic Properties of Gas Phase Species of Importance to Ozone Depletion - JANAF Thermochemical Tables for Some Chlorine Oxides"; J. Phys. Chem. Ref. Data.; (submitted).

Chemical Kinetics Data Evaluation Activities  
In Support of the NASA Upper Atmosphere Research Program

R. F. Hampson

Chemical Kinetics and Thermodynamics Division  
National Institute of Standards and Technology (NIST)

Gaithersburg, MD 20899

Objective

To provide the reliable, evaluated reaction rate data base required as input data for large scale modeling efforts which provide the basis for our understanding of atmospheric chemistry.

Summary of Progress and Results

The principal investigator has participated in the data evaluation activities of the NASA Panel for Data Evaluation on which panel he has the primary responsibility to review and evaluate the rate data for reactions of halogen-containing species. Updated and reevaluated data bases were presented at panel meetings held in February, May, and September, 1991.

The principal investigator also participated in the data evaluation activities of the IUPAC Commission on Chemical Kinetics Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. Updated and reevaluated data bases were presented at meetings of the Subcommittee held in October, 1990 and May, 1991.

Publications

W. B. DeMore, D. M. Golden, R. F. Hampson, C. J. Howard, M. J. Kurylo, M. J. Molina, A. R. Ravishankara, and S. P. Sander, "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling", Evaluation No. 9 of the NASA Panel for Data Evaluation, JPL Publication 90-1, Jet Propulsion Laboratory, Pasadena, CA, January, 1990.

R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, and J. Troe, "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement IV", IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, submitted for publication in Journal of Physical and Chemical Reference Data.

DATA SURVEY AND EVALUATION  
464-41-04  
W. B. DeMore  
Jet Propulsion Laboratory

This task supports JPL participation in the NASA Panel for Data Evaluation:

Chairman: W. B. DeMore, Jet Propulsion Laboratory

Panel Members: D. M. Golden, SRI International  
R. F. Hampson, National Institute of Standards  
and Technology  
C. J. Howard, NOAA Environmental Research Laboratory  
C. Kolb, Aerodyne Research Inc.  
M. J. Kurylo, National Institute of Standards  
and Technology  
M. J. Molina, Massachusetts Institute of  
Technology  
A. R. Ravishankara, NOAA Environmental Laboratory  
S. P. Sander, Jet Propulsion Laboratory

Objectives:

The purpose of this task is to maintain an updated set of evaluated rate constants and photochemical cross-sections for use in stratospheric modeling, and to publish the evaluated data in a form accessible to the community of atmospheric scientists.

Progress and Results:

Preparations have begun for publication of Evaluation Number 10, which is scheduled for publication in January of 1992. A new member, Dr. C. Kolb, has joined the Panel and will have responsibility for the section on heterogeneous processes.

Publications:

A series of nine evaluations has been published since 1977, the most recent being Evaluation Number 9, January, 1990, JPL Publication 90-1.

# A Computational Investigation of Reactive Species

Donald H. Phillips  
NASA, Langley Research Center  
and  
Charles F. Jackels  
Wake Forest University

## Abstract of Objectives

The highly reactive molecules which are involved in the catalytic ozone destruction chemistry are difficult to investigate experimentally over the full temperature and pressure range of interest in the atmosphere. The objective of this research is to supplement experimental results with information from computational determinations of properties of the reactive species and of the outcome of processes involving these species. This includes the stability of weakly bound complexes which may be important at the temperatures of the tropopause and of polar regions in the winter; the investigation of photolysis processes, especially the prediction of photolysis products; and the investigation of reaction intermediates and mechanisms to enable greater confidence in the extrapolation of experimental results to temperatures and pressures outside the experimental range.

## Summary of Progress and Results

An investigation of the frequencies and intensities of the vibrational transitions of the covalently bonded  $HO\cdots OH$  molecule has been completed. The results provide a basis for identifying this compound in the lower stratosphere and polar stratosphere if it exists there. Computations on the vibrational frequencies of the hydrogen bonded complex  $HO \cdots OOH$  are nearly complete.

This information will be useful in the evaluation of the reaction mechanism for the bimolecular reaction between  $OH$  and  $HO_2$ .

The vibrational frequencies for the complex between  $H_2O$  and  $CO_2$  were determined during an industrial sabbatical by one of the investigators. The results, along with the intensity of the transitions which are yet to be calculated, are of interest with respect to the greenhouse effect.

Calculations on several hypervalent compounds ( $Cl_xO_y$ ) and the bicarbonate radical ( $HO \dots CO_2$ ) have not been brought to a satisfactory conclusion. Apparently it is necessary to include more orbitals than practical in a complete-active-space (CAS) multiple-configuration self-consistent-field (MCSCF) treatment in order to obtain a reliable wave function. A somewhat old fashioned approach using natural orbitals from small configuration interaction (CI) treatments may be attempted for these systems.

### Journal Publications

Ground and Excited States of Methyl Peroxy,  $CH_3O_2$ , Radical: A Computational Investigation, J. A. Jafri and Donald H. Phillips, Journal of the American chemical Society, vol 112, pp2586 -2590(1990)

- A. Title of Research Task: Upper Atmosphere Data Program (UADP)
- B. Investigator/Institution: Robert K. Seals, Jr.  
Atmospheric Sciences Division  
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- C. Abstract of Research Objectives: Rapid, effective access to the increasing volume of data on stratospheric trace gases is important in advancing our knowledge of the Earth's atmosphere. These data are derived from a variety of sources, ranging from satellite experiments and multi-dimensional model calculations to individual balloon measurements. This task focuses on the development, operation, and maintenance of an electronic data base for such data with particular emphasis on two-dimensional data sets from models and satellite measurements. The objective is to serve the atmospheric science community by providing convenient access to data, by providing data display and manipulation capabilities and by supporting special intercomparison and atmospheric assessment activities.
- D. Summary of Progress and Results: Data areas of emphasis have been the development of a trace gas climatology for use in Upper Atmosphere Research Satellite (UARS) investigations and the enhancement of UADP data holdings. A trace gas climatology data set has been developed for use by the UARS CLAES, HALOE, ISAMS, and MLS teams. The data set combines existing global zonal mean measurement data for temperature, O<sub>3</sub>, H<sub>2</sub>O, HNO<sub>3</sub>, CH<sub>4</sub>, and N<sub>2</sub>O with calculations from a Lawrence Livermore National Laboratory two-dimensional atmospheric model to provide a 1-year monthly zonal mean global climatology of the UARS measurement and interferent trace gases. A pre-launch version of the climatology for temperature and 18 trace gases has been delivered to the UARS Project. Also, existing LIMS, SAMS, and SBUV satellite data holdings have been transformed onto a standard model intercomparison latitude-pressure grid. This allows direct comparisons and manipulations of model and measurement data and will facilitate upcoming model-data validation activities. In addition, a large number of new model prediction results from various modeling groups have been added, and work to incorporate SAGE II H<sub>2</sub>O data has begun.

In the data system area, emphasis has been on increasing the efficiency of the UADP data access system, developing a portable version of the UADP data base for use at workshops, and providing additional data manipulation and display capabilities. A new file-oriented data access approach has been implemented which provides greater than a tenfold improvement in data access speeds for two-dimensional data sets. It also incorporates a common file format which is used for storage of our two-dimensional data sets and provides a uniform basis for UADP data submission and distribution. The portable version of the data base system has been implemented based on SUN workstations with rewriteable optical disks. This portable version was developed particularly to support



workshop activities and includes a broad range of data manipulation and display capabilities, including color hard copy. The system has already demonstrated its utility in support of a 1991 workshop on the Atmospheric Effects of Stratospheric Aircraft. In the manipulation and display area, the capability to provide sums, differences, ratios, or integrations of data files has been implemented. Multiple frame color display software has been developed and used to generate a color atlas of the LIMS, SAMS, and SBUV satellite data holdings.





